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Quenching of the $He_\mu{}^+(2s)$ atom

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Quenching of the metastable $2s$ state of the $He_\mu{}^+$ atom in helium gas is discussed. The first part of the discussion, which is devoted entirely to processes occurring after the $He_\mu{}^+$ has become bound to one or more ordinary helium atoms, is based partly on Cohen's calculations of rates of vibrational quenching and partly on estimates obtained in the present paper of rates of Burbidge—de Borde quenching and Ruderman quenching. It is concluded that Burbidge—de Borde quenching or Ruderman quenching, or both, are likely to be more effective than Cohen quenching if the vibrational level of the bound system is low. A recent experiment by von Arb *et al.* is then analyzed in the light of this conclusion. The analysis is based on the reported absence, or near absence, of Auger electrons accompanying $2s$ quenching. While it is agreed that the Cohen mechanism occurring in the molecular ion $HeHe_\mu{}^+$ remains the most likely explanation of the experiment, it is concluded that the quenching occurs in comparatively high levels. It is then argued that this conclusion is in accord with some theoretical investigations of three-body association reactions and also with some elementary considerations regarding the relaxation of highly excited diatomic molecules, and it is further concluded that the quenching is most likely to occur in states with very low rotational quantum number and vibrational quantum number $8 \le v \le 14$.

I. INTRODUCTION

Cohen has argued that the $He_\mu{}^+(2s)$ atom, which is a positive muonic helium ion in the metastable $2s$ state, should be rapidly quenched if it becomes bound to one or more helium atoms.[1] Furthermore, some recent measurements by von Arb *et al.* in helium gas at pressures between 50 and 600 torr have established that molecular ion formation followed by quenching does in fact occur after a $He_\mu{}^+(2s)$ is formed.[2] The arguments presented by Cohen are very appealing, not only because the mechanism involved, a $2s \rightarrow 2p$ muonic Stark transition induced by molecular vibrations and quickly followed by a $2p \rightarrow 1s$ radiative transition, had apparently not been previously considered, but also because some detailed expressions for the quenching rate, which were given in the harmonic-oscillator approximation for diatomic and triatomic molecular ions, have a form that appears to be more or less easily generalized to almost any molecule or cluster of which a muonic helium ion might conceivably become a constituent, an important consideration because the details of the entire sequence(s) of chemical and molecular processes undergone by a $He_\mu{}^+$ ion in helium are not yet fully understood, especially at high densities.[3–5] In the harmonic-oscillator approximation, which is adequate in very low vibrational levels, the Cohen rate varies linearly with terms of the form $(v+\frac{1}{2})\omega^3$, where v and ω are a vibrational quantum number and frequency. When computed more precisely, this rate has its largest values in vibrational levels that are moderately high. It was shown in Ref. 1 that the Cohen rate in the diatomic molecular ion $HeHe_\mu{}^+$ is largest in levels with $5 \le v \le 8$.

The primary purpose of the present paper is to argue that the Cohen mechanism is likely to be the dominant quenching process only in comparatively high vibrational levels. Some calculations are presented which indicate that quenching of the $2s$ state in low vibrational levels should be due primarily to one or both of two other mechanisms that have been known for many years to be operative in isolated muonic atoms. One of these mechanisms, which was proposed by Burbidge and de Borde[6] and which was briefly discussed for an isolated, neutral muonic helium atom by Cohen and Bardsley,[7] is a $2s \rightarrow 1s$ monopole Auger transition. The other, which was proposed by Ruderman,[8] is more or less similar to the Cohen mechanism, the essential difference being that the $2s \rightarrow 2p$ muonic Stark transition is induced by coupling to the motion of individual electrons rather than to molecular vibrations. Because neither of these processes appears to be calculable for molecules in both the relatively precise and the readily generalized way achieved in the harmonic-oscillator approximation by Cohen for vibrational quenching, the arguments outlined in the present paper are based on estimates for special cases, with some previous discussions of $He_\mu{}^+(2s)$ quenching—not only the one by Cohen[1] but also the paper by Carboni and Pitzurra[4]—being decisive in the selection of these special cases.

A certain amount of the discussion in the present paper is motivated by the suggestion made in Ref. 4 that the very low amount of Stark quenching reported in Ref. 3 might be accounted for if ordinary helium atoms become clustered symmetrically about the $He_\mu{}^+(2s)$. It acknowledged, however, that the very existence of symmetric clusters composed of three or more ordinary helium atoms is questionable because, as pointed out by Cohen,[1] a calculation performed by Milleur *et al.*[9] for a number of symmetric clusters of the type He_nH^+, which should each have a potential surface nearly identical to that for a similar cluster of the type $He_nHe_\mu{}^+$, has shown that the planar He_3H^+ and the tetrahedral He_4H^+ are both relatively less stable than the linear He_2H^+. But because the calculations reported in Ref. 9 appear to admit the possibility that the computed minima in the energies of these symmetric configurations of He_3H^+ and He_4H^+ could be true local minima (as opposed to saddle points), we have chosen to investigate some of the implications of the assumption that symmetrically structured $He_nHe_\mu{}^+$ molecules with $n \geq 3$ could indeed be formed.

In Sec. II the Burbidge–de Borde rate is shown to be nearly three times larger than the Cohen rate in the lowest level of the diatomic ion $HeHe_\mu{}^+$ and about seven times larger than the Cohen rate in the lowest level of the triatomic ion $He_2He_\mu{}^+$. Section II also includes a brief comment on the possible occurrence of Ruderman quenching in more complex molecules. This comment is based on some exceedingly rough estimates of the Ruderman rate obtained in the appendix for the rather special and not very realistic case of a $He_\mu{}^+(2s)$ atom situated a fixed distance from a single, initially undistorted helium atom. The very approximate numerical results obtained in the appendix provide the basis for arguments made there that Ruderman quenching is likely to be at least as important as the Cohen mechanism in low vibrational levels, including those of any symmetrically structured ion of the type $He_nHe_\mu{}^+$ with $n \geq 3$. The relevance of our numerical results to experiment is discussed in Sec. III, where it is concluded that the quenching observed by von Arb *et al.*, though indeed due to the Cohen mechanism in $HeHe_\mu{}^+$, occurs in high or moderately high levels of this molecule. It is then argued that this conclusion is in accord with some theoretical investigations of three-body association reactions and also with some elementary considerations regarding the relaxation of highly excited diatomic molecules, and it is further concluded that the quenching is most likely to occur in states with very low rotational quantum number and vibrational quantum number $8 \leq v \leq 14$.

II. BURBIDGE–de BORDE QUENCHING

The rate of Burbidge–de Borde quenching in the $He_\mu{}^+(2s)$ atom will be denoted by γ_B. With the Coulomb distortion of the final electron wave function taken into account, this rate is given by $\gamma_B = 1.74\times 10^8(\rho/\rho_0)$ sec^{-1}, where ρ is the initial electron density at the site of the very small muonic helium ion and ρ_0 is the electron density at the center of an ordinary hydrogen atom.[6,7]

A. Diatomic molecule

The rate γ_B was estimated for a $He_\mu{}^+$ atom bound in a $HeHe_\mu{}^+$ molecule by using a very approximate but very simple electron wave function for the HeH^+ ion computed many years ago by Coulson and Duncanson.[10] For a given value of the internuclear separation, the electron wave functions for $HeHe_\mu{}^+$ and HeH^+ molecules should be nearly identical because, as noted by Cohen and Bardsley in a discussion of collisional quenching, the interaction of a normal He atom with $He_\mu{}^+$ is essentially the same as with H^+ except at very small separations.[7] Because the Coulson-Duncanson wave function was determined for the equilibrium configuration of HeH^+, using it to compute γ_B is likely to be an acceptable procedure only if the $HeHe_\mu{}^+$ is in a low vibrational level, where the internuclear separation is restricted to a relatively narrow range centered on its equilibrium value. The rate obtained with this function is $\gamma_B = 1.5\times 10^8$ sec^{-1}, which is nearly three times larger than the Cohen rate in the lowest vibrational level of $HeHe_\mu{}^+$ but less than half its values in levels with $4 \leq v \leq 9$. Although more accurate wave functions for the HeH^+ molecule have been computed,[11] we believe that the value of γ_B obtained with the Coulson-Duncanson function should be adequate for the purposes of the discussion presented in Sec. III.

B. Triatomic molecule

The rate γ_B was estimated for a $He_\mu{}^+$ atom bound in a $He_2He_\mu{}^+$ molecule by using a rather accurate electron wave function for the equilibrium configuration of the He_2H^+ ion computed by Poshusta and Siems.[12] The equilibrium configuration of the He_2H^+ molecule is linear and symmetric. The Poshusta-Siems wave function consists of 30 valence-bond configurations constructed from 15 orbitals. It will be denoted by Ψ_{PS}. The function Ψ_{PS} was described in a Cartesian coordinate system, with the origin situated at the site of the $He_\mu{}^+$ atom and the z axis coinciding with the molecular axis of symmetry.[13] The calculations consisted of evaluating the integrals

$$N = \int |\Psi_{PS}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)|^2 d\tau_1 d\tau_2 d\tau_3 d\tau_4 , \tag{1}$$

$$\rho = 4\int |\Psi_{PS}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4=0)|^2 d\tau_1 d\tau_2 d\tau_3 , \tag{2}$$

where N is the normalization of Ψ_{PS} and ρ is the total probability density for one or another of the electrons to be at the center of the molecule. The normalization was computed as a check on the accuracy of the calculations.

Because there is no need to know γ_B with great precision, the integrations of Ψ_{PS} were performed using the Monte Carlo method; and because no integrations were performed analytically, the orbitals were expressed directly in terms of hydrogenic functions (with polarization factors) rather than the linear combinations of gaussians employed by Poshusta and Siems, thereby reducing the amount of computer time required. In computing N and ρ, only that part of Ψ_{PS} was considered which corresponds to all four electrons being somewhere within a box specified by

$$-R_b < x < R_b, \quad -R_b < y < R_b, \quad -R_s - R_b < z < R_s + R_b , \tag{3}$$

where R_b is an adjustable parameter and $R_s = 1.764$ a.u. is the equilibrium spacing for He_2H^+, as determined by Poshusta and Siems. The value of R_b was chosen by requiring the computed value of N to be reasonably close to unity and to be obtainable with acceptable accuracy by taking into account a not unreasonably large number of randomly selected electron configurations. Since the accuracy of a Monte Carlo integration can depend sensitively on the choice of random number density,[14] the randomly selected positions of each electron were assumed to have a distribution of the form

$$p(\mathbf{r})=p_\alpha(x)p_\alpha(y)p_\beta(z)\ , \tag{4a}$$

where

$$p_\alpha(x)=a_\alpha \exp(-b\,|x\,|),\quad -R_b<x<R_b\ , \tag{4b}$$

$$\int_{-R_b}^{+R_b} p_\alpha(x)dx=1\ , \tag{4c}$$

and

$$p_\beta(z)=a_\beta,\quad -R_s<z<R_s\ , \tag{4d}$$

$$p_\beta(z)=a_\beta \exp[-b(\,|z\,|-R_s)],\quad R_s<|\,z\,|<R_s+R_b\ , \tag{4e}$$

$$\int_{-R_s-R_b}^{+R_s+R_b} p_\beta(z)dz=1 \tag{4f}$$

with a_α and a_β being normalization factors and b a parameter chosen to enhance the efficiency of the Monte Carlo integration.

For a given number of randomly selected electron configurations, the accuracy of the integrations were found to vary dramatically with b. The most accurate calculations were obtained with $b\simeq 2.0$ a.u.$^{-1}$. It was found that choosing $b=2.0$ a.u.$^{-1}$ and $R_b=3.0$ a.u. and taking into account 10^5 randomly selected configurations resulted in the computed values of the normalization and the quenching rate being $N=0.954\pm0.014$ and $\gamma_B=(5.51\pm0.05)\times10^7$ sec^{-1}, where the errors are Monte Carlo estimates of the standard deviations. Our value of γ_B, which could probably be improved slightly by dividing it by our value of N, is about seven times larger than Cohen's estimate of the vibrational quenching rate in the lowest level of $He_2He_\mu^+$. As with the diatomic molecule, this value of γ_B is likely to be reliable only in low levels.

C. More complex molecules

Our values of γ_B relative to the Cohen rate in low levels of $HeHe_\mu^+$ and $He_2He_\mu^+$, especially our determination that γ_B is relatively even larger in the latter than the former, suggest that Burbidge–de Borde quenching might also be important in low vibrational levels of more complex structures. Of course, for a cluster consisting of one or more helium atoms loosely attached by long-range forces to a tightly bound triatomic core—and, on the basis of energy considerations, this is arguably the form that such systems would assume[1,9]—the value of γ_B for $He_2He_\mu^+$ can be employed with a certain degree of confidence in a discussion of low vibrational levels. However, as argued in Sec. I, there appears to be at least a possibility that the molecules $He_3He_\mu^+$ and $He_4He_\mu^+$ can exist, though surely not indefinitely, in symmetric configurations with the muonic helium ion at the center. Therefore, some discussion should be devoted to the nature of any $2s$ quenching that might occur in these structures. Our value of γ_B for the triatomic molecule would clearly be inappropriate for such molecules. Nevertheless, no attempt was made to estimate γ_B for these ions, even though such calculations are feasible. It was decided that the length and complexity of the numerical work would not be justified by our present knowledge of the roles played by these molecules: there is, at least in our judgement, no compelling reason to believe that symmetric configurations of $He_3He_\mu^+$ and $He_4He_\mu^+$ are indeed formed in appreciable numbers, though as noted briefly in Sec. III C 2 this possibility cannot be totally excluded in a high-density gas; and furthermore, even if they are formed, their binding energies relative to that of the $He_2He_\mu^+$ molecule[1,9] are such that there is no compelling reason to believe that such a molecule would retain its original symmetric structure over a sufficiently long period of time, especially in a high-density gas. But even if Burbidge–de Borde rates were computed for these molecules and found to be comparatively small in low vibrational levels—and we are unconvinced that this would be the case—the total dominance of vibrational quenching can still be questioned because, as argued in the appendix on the basis of some very approximate calculations requiring comparatively little numerical work, the Ruderman rate seems likely to be at least comparable to the Cohen rate in low-lying levels.

III. RELEVANCE TO EXPERIMENT

The experimental results of von Arb *et al.*[2] show that the rate λ_Q of pressure-dependent quenching of the $He_\mu^+(2s)$ atom in helium gas has a nearly quadratic behavior between 50 and 600 torr. The pressure dependence of λ_Q was fitted rather accurately to the empirical formula

$$\lambda_Q=k_1\rho_{He}+k_2\rho_{He}^2\ , \tag{5a}$$

$$k_1=(1.5\pm0.6)\times10^{-13}\ \mathrm{cm^3\,sec^{-1}}\ , \tag{5b}$$

$$k_2=(5.9\pm0.8)\times10^{-32}\ \mathrm{cm^6\,sec^{-1}}\ , \tag{5c}$$

where ρ_{He} is the number density of helium atoms. Except for the total effect of the pressure-independent processes of muon decay and $2s\rightarrow1s$ two-photon emission, which is known with precision and which becomes dominant only at pressures less than approximately 50 torr, almost all contributions to the $2s$ disappearance rate were found to be accompanied by a K_α x ray, though it was noted that the possibility of a small amount of nonradiative quenching due to an Auger process cannot be excluded. von Arb *et al.* interpreted their results as indicating that Cohen quenching occurs in the $HeHe_\mu^+$ molecule, but no conclusion was stated with regard to the vibrational levels in which the quenching occurs. It was noted that the data are consistent with the rate coefficient for the three-body association reaction

$$He_\mu^+ + He + He \rightarrow HeHe_\mu^+ + He \tag{6}$$

being equal at room temperature to the value of k_2 specified by Eq. (5c), in close agreement with an experimentally determined value[15] of the rate coefficient for the somewhat similar reaction

$$He^+ + He + He \rightarrow He_2^+ + He\ . \tag{7}$$

It was also noted in Ref. 2 that the term $k_1\rho_{He}$ in Eq. (5), which is the dominant contribution to λ_Q only at pressures less than approximately 100 torr, is an order of magnitude higher than predicted by calculations of collisional quenching of the $He_\mu^+(2s)$ atom.[7]

A. Absence of Auger quenching

We agree with the conclusions of von Arb *et al.;* but because of the relative values of our estimate of the Burbidge—de Borde rate (1.5×10^8 sec^{-1}) and Cohen's estimate of the vibrational quenching rate (5.7×10^7 sec^{-1}) in the lowest level of $\mathrm{HeHe}_\mu{}^+$, we believe that the reported absence, or near absence, of Auger quenching of the $2s$ state indicates that the observed quenching occurs in comparatively high levels where the Cohen rate is larger and where the Burbidge—de Borde rate is likely to be smaller. In high and moderately high vibrational levels, the internuclear separation tends to be larger than the equilibrium separation because of the increased importance of the anharmonicity of the molecular potential, and Burbidge—de Borde quenching should, therefore, be of diminished importance since the adiabatically varying electron density at the site of the $\mathrm{He}_\mu{}^+$ atom should, on average, be smaller than in the lowest level.

There is, of course, another conceivable explanation of the absence, or near absence, of Auger quenching of the $2s$ state. It might be argued that Ruderman quenching, which would be experimentally indistinguishable from Cohen quenching, could be important. Although the estimates of the Ruderman rate obtained in the appendix and shown there by the curve in Fig. 4 are probably accurate enough to rule out this mechanism in high and moderately high levels of $\mathrm{HeHe}_\mu{}^+$, where the internuclear separation is, on average, comparatively large, the approximations employed in obtaining this curve are, in our judgement, not good enough to permit a reliable estimate for low levels. However, for reasons outlined in the appendix, we believe that another estimate of this rate, the single value obtained using Ruderman's approximation for an isolated atom and shown in Fig. 4 at zero internuclear separation, should be a reasonably reliable upper limit to the actual rate in low levels of $\mathrm{HeHe}_\mu{}^+$. Therefore, Ruderman quenching in low levels of this molecule should, at the very most, not be significantly more important than the Burbidge—de Borde process, and our conclusion about Cohen quenching occurring in comparatively high levels should be unaffected. We must also add that none of the estimates of the Ruderman rate obtained in the appendix gives any encouraging indication that this process could account for the very large measured value of k_1 reported in Ref. 2.

B. Formation and relaxation of $\mathrm{HeHe}_\mu{}^+$

If our conclusion about the relative importance of the various quenching mechanisms in low levels of $\mathrm{HeHe}_\mu{}^+$ is correct, it is necessary that this molecule be formed initially in sufficiently high levels and afterwards never reach a low level; and because the nearly quadratic pressure dependence of λ_Q between 50 and 600 torr implies that reaction (6) is the rate-determining process in the sequence of events leading ultimately to $2s$ quenching in $\mathrm{HeHe}_\mu{}^+$, it is also necessary that both the vibrational quenching in a comparatively high level and any molecular relaxation preceding it occur at rates sufficiently faster than the rate of this reaction. Since vibrational quenching is pressure independent and molecular relaxation should vary only linearly with the pressure, the constraints on the rates of these two processes will be satisfied if they are satisfied at 600 torr. To be more specific, quenching and all relaxation preceding it at 600 torr must both occur at rates at least several times faster than 2.5×10^7 sec^{-1}, which is the measured value of λ_Q at this pressure. The fulfillment of these two conditions would also mean that the three-body association reaction

$$\mathrm{HeHe}_\mu{}^+ + \mathrm{He} + \mathrm{He} \rightarrow \mathrm{He}_2\mathrm{He}_\mu{}^+ + \mathrm{He}\ , \tag{8}$$

which can reasonably be expected to have a rate coefficient not greatly different from that for reaction (6), is unlikely to complicate matters at pressures less than 600 torr by taking place before quenching occurs. We believe this last point to be significant because the somewhat similar reaction

$$\mathrm{He}_2{}^+ + \mathrm{He} + \mathrm{He} \rightarrow \mathrm{He}_3{}^+ + \mathrm{He} \tag{9}$$

has been reported to occur at low temperatures at a rate faster than that of reaction (7).[16] As outlined below, there are strong indications that all of the conditions outlined above are satisfied, though our arguments about molecular relaxation are more qualitative than quantitative.

To our knowledge, a detailed theoretical study of reaction (6) has not been performed; but there is a recent theoretical analysis[17] of a very careful experimental study by Johnsen, Chen, and Biondi[18] of reaction (7). The calculations described in Ref. 17 reproduce rather satisfactorily the temperature dependence of the experimentally determined rate coefficient reported in Ref. 18, though the computed magnitude is between 10% and 20% too low. (It must be noted, however, that the value given by Johnsen *et al.*[18] for the rate coefficient at room temperature is about twice as large as the one reported by de Vries and Oskam.[15]) According to the calculations outlined in Ref. 17, the $\mathrm{He}_2{}^+$ molecule is most likely to be formed initially at normal temperatures in a very high vibrational level with relatively high angular momentum. These calculations, which were performed using classical mechanics, indicate that the initial vibrational quantum number of the $\mathrm{He}_2{}^+$ should be usually in the range $12 \le v \le 22$, with the initial rotational quantum number in the range $0 \le K \le 25$. More specifically, for a given value of the initial angular momentum, the initial vibrational level appears likely to be one of the four or five highest possible. It therefore seems reasonable to assume that much the same would be true of the $\mathrm{HeHe}_\mu{}^+$ molecule formed in reaction (6), though the highest possible value of v for a given value of K should be somewhat smaller because of the shorter range of the molecular potential. It must be added that the investigation reported in Ref. 17 is not the only one that can be cited in support of this conjecture. A theoretical study conducted many years ago by Keck showed that the production of H_2, O_2, and I_2 molecules at normal temperatures in three-body association reactions of a somewhat simpler nature than reactions (6) and (7) usually involves an energy transfer less than $kT/2$, which would imply that these molecules, too, are formed initially in very high vibrational levels.[19]

To our knowledge there has been no experimental or theoretical investigation of the collisional deexcitation of very highly excited states of either $\mathrm{He}_2{}^+$ or $\mathrm{HeHe}_\mu{}^+$. However, investigations of relaxation processes in other molecules indicate that the size of the relevant energy spacing should play a crucial role.[20,21] If the spacing is at least moderately large compared to the initial translational energy, the probability of deexcitation in a single collision is likely to be small because the relative change required in the translational momentum should be quite large. A large energy spacing can also mean that the collision is nearly adiabatic, which also diminishes the probability of deexcitation. To a very rough approximation, the adiabaticity of an inelastic collision involving an energy change ΔE is determined by the parameter

$$\xi = R_I \,|\,\Delta E\,|\,/(2\pi\hbar V_R)\ , \tag{10}$$

where R_I is an estimate of the range of the interaction between the colliding molecules and V_R is their relative velocity.[20] A collision is likely to become increasingly adiabatic as ξ becomes increasingly larger than unity. Although in general adiabatic effects do not necessarily accompany large momentum changes, and vice versa, the dimensionless quantities $|\,\Delta E\,|\,/(kT)$ and ξ are numerically equal for $\mathrm{HeHe}_\mu{}^+$ molecules in helium gas at $T=300$ K if the interaction range appearing in Eq. (10) is assigned the not unreasonable value $R_I=5$ a.u. For this reason, though we shall quote only values of $\Delta E/(kT)$ in the following discussion, it should be understood that we believe adiabatic effects are very likely also to be present if the energy spacing involved in a given transition is large enough to suggest that the required momentum change could be an inhibiting factor. Furthermore, if the energy spacing is considerably smaller than or (perhaps) even roughly equal to the initial translational energy, the required change in the relative momentum is much less likely to diminish the probability of a transition, and such collisions are also unlikely to be adiabatic.

Some numerical data relevant to the formation, relaxation, and vibrational quenching of highly excited states of $\mathrm{HeHe}_\mu{}^+$ are presented in Table I and Figs. 1 and 2. Table I lists estimates of vibrational energy levels if the rotational quantum number is zero. These estimates were obtained using the JWKB approximation and are given in units of kT, with $T=300$ K. Table I also lists values of the maximum internuclear separation $R_{\max}$ for each of these levels, as obtained by equating $R_{\max}$ to the larger of the classical turning points. Results are listed for two assumed forms of the molecular potential. In one instance, the potential is assumed to be of the usual Morse type, with parameters $D_M=0.073$ hartrees, $R_e=1.47$ a.u., and $\beta=1.47$ a.u.$^{-1}$, which are the values employed by Cohen in some of his calculations.[1] This potential will be denoted by V_M. The vibrational quenching rates obtained by Cohen with this potential are also listed in Table I.[22] In the other instance, the potential is assumed to be the sum of V_M and a term V_{LR}, which is given in atomic units by

$$V_{\mathrm{LR}}(R)=G(R)(C_2/R^4)\ , \tag{11a}$$

$$G(R)=\begin{cases}1-\exp[-C_1(R-R_e)^N], & R>R_e\\ 0, & R<R_e\end{cases} \tag{11b}$$

$$C_1=0.005,\ \ C_2=-0.692,\ \ N=4\ , \tag{11c}$$

TABLE I. Estimates of the energy E_v and the maximum internuclear separation $R_{\max}$ for all states of the $\mathrm{HeHe}_\mu{}^+$ molecule with rotational quantum number $K=0$ and vibrational quantum number $v\geq 7$, as obtained with the JWKB approximation. Results are presented for two assumed forms of the molecular potential, V_M and $V=V_M+V_{\mathrm{LR}}$, where V_M is the Morse potential employed by Cohen (Ref. 1) and V_{LR}, which is specified by Eq. (11), is a correction taking into account approximately the presence of the long-range ion-induced dipole interaction. Energies are given in units of kT, with $T=300$ K. Estimates of the vibrational quenching rate obtained by Cohen with the potential V_M are also listed.

	Molecular potential V_M			Molecular potential $V=V_M+V_{\mathrm{LR}}$	
v	E_v/kT ($T=300$ K)	$R_{\max}$ (a.u.)	Vibrational quenching rate[a] (sec^{-1})	E_v/kT ($T=300$ K)	$R_{\max}$ (a.u.)
19				-4×10^{-7}	206
18				-2×10^{-3}	24
17				-0.03	12.7
16				-0.14	8.59
15	-0.02	7.57	0.2×10^{8}	-0.44	6.66
14	-0.49	5.39	0.8×10^{8}	-1.01	5.48
13	-1.58	4.59	1.3×10^{8}	-2.03	4.66
12	-3.30	4.08	1.9×10^{8}	-3.65	4.12
11	-5.64	3.71	2.3×10^{8}	-5.91	3.73
10	-8.60	3.42	2.7×10^{8}	-8.80	3.43
9	-12.19	3.17	3.1×10^{8}	-12.34	3.18
8	-16.40	2.96	3.3×10^{8}	-16.51	2.96
7	-21.23	2.77	3.5×10^{8}	-21.31	2.77

[a] Reference 1.

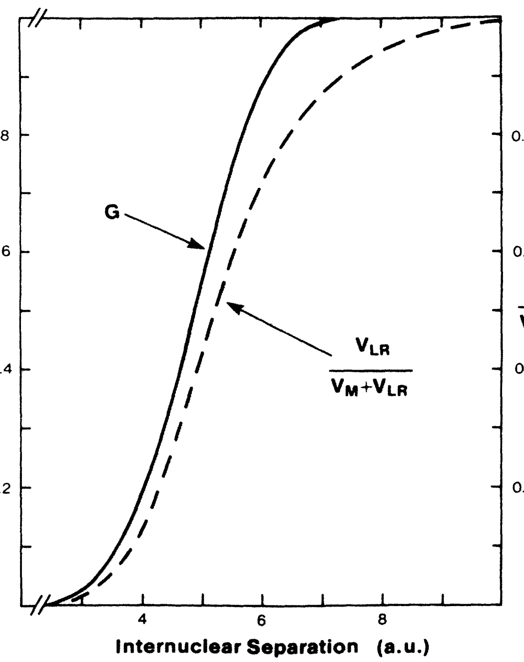

FIG. 1. Dimensionless function G and the relative contribution of V_{LR} to the potential $V=V_M+V_{\text{LR}}$, where V_M is a Morse potential and V_{LR} is a correction taking into account the long-range ion-induced dipole interaction. The scale is the same for both curves.

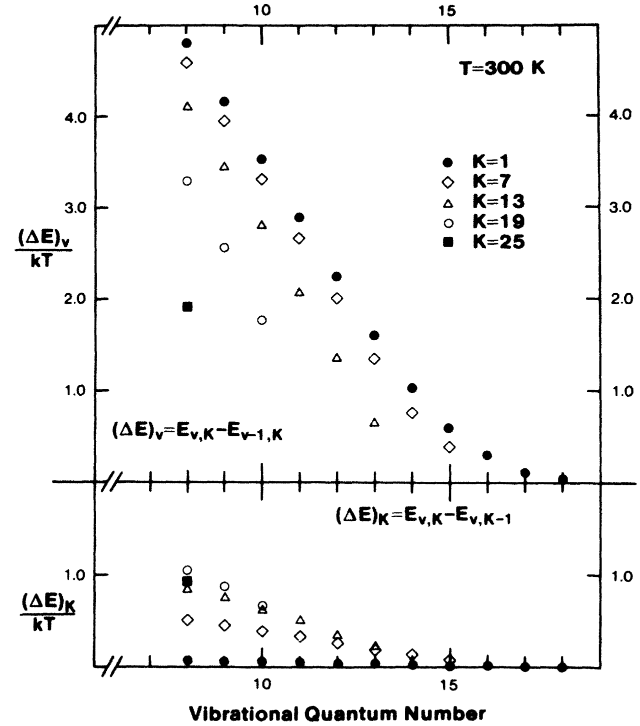

FIG. 2. Some estimates of $(\Delta E)_K = E_{v,K} - E_{v,K-1}$ and $(\Delta E)_v = E_{v,K} - E_{v-1,K}$, where $E_{v,K}$ is the energy of a $\text{HeHe}_\mu{}^+$ molecule with vibrational quantum number v and rotational quantum number K. These energy differences, which are shown in units of kT with $T=300$ K, were obtained for the potential $V=V_M+V_{\text{LR}}$ by using the JWKB approximation to compute values of $E_{v,K}$. The term V_M in the expression for V is a Morse potential, while V_{LR} is a correction taking into account the long-range ion-induced dipole interaction. Results are given for all states with $v \geq 8$ and $K=1$, 7, 13, 19, and 25.

where R is the internuclear separation. This potential will be denoted by V. The contribution to V specified by Eq. (11) is an *ad hoc* expression designed to take into account approximately the long-range ion-induced dipole interaction, which is believed to play a role in reaction (7).[17,23,24] For very large separations, where V_M is relatively quite small, the term V_{LR} is an accurate representation of the long-range interaction, which depends only on the internuclear separation and the polarizability of the helium atom.[25] For comparatively small separations, its form is chosen so that it decreases rapidly and smoothly to negligible values at separations where V_M should be more or less adequate. Figure 1 shows the relative contribution made by the term V_{LR} to the potential $V=V_M+V_{\text{LR}}$. It also shows the function G defined in Eq. (11). In the limited range of separations where V_{LR} and V_M are of comparable magnitude, the actual molecular potential is probably not represented with great precision, but we believe this should not affect the conclusions of the present paper. Some additional calculations performed for several other sets of reasonable values of the parameters C_1 and N appearing in Eq. (11b) gave results that were, in most instances, not very different from those listed in Table I.[26]

It is apparent from Table I that the long-range ion-induced dipole interaction causes a few additional vibrational levels to be present, all of them loosely bound and with comparatively large values of $R_{\max}$, though we note that some additional calculations not reported here in any detail show, not surprisingly, that the importance of the term V_{LR} becomes less pronounced as the rotational quantum number increases. To the extent that the calculations reported in Ref. 17 are applicable to reaction (6), a sizeable fraction of the $\text{HeHe}_\mu{}^+$ molecules should be initially formed in such loosely bound and finely spaced states, with the remainder being formed in states only slightly less highly excited. We have not computed vibrational quenching rates for the potential $V=V_M+V_{\text{LR}}$, but a comparison of the binding energies and the maximum separations listed in Table I for the potentials V_M and V suggests that, for a given value of v, the rate for the corrected potential V is unlikely to be very different from Cohen's estimated rate for the Morse potential if the latter rate is approximately 10^8 sec^{-1} or greater. Therefore, the values of the Cohen rate listed in Table I indicate that in most instances a certain amount of deexcitation must first take place if quenching is to occur at a rate sufficiently faster than that of reaction (6); and this deexcitation must, of course, occur sufficiently quickly.

For almost all of the states likely to be formed initially in reaction (6), the energy differences involved in the most favored collisional deexcitation should, at the very most, not be much larger than thermal energies. This is illustrated in Fig. 2, which shows some values of the energy differences,

$$(\Delta E)_K = E_{v,K} - E_{v,K-1}\ , \tag{12a}$$

$$(\Delta E)_v = E_{v,K} - E_{v-1,K}\ , \tag{12b}$$

where $E_{v,K}$ is the energy of the level with vibrational quantum number v and rotational quantum number K. The energy differences shown in Fig. 2, which are given in units of kT with $T=300$ K, were obtained for the potential $V=V_M+V_{\mathrm{LR}}$ by employing the JWKB approximation. As might be expected, these energy differences suggest that the initial deexcitation of the $\mathrm{HeHe}_\mu{}^+$ is most likely to proceed by transitions between states with the same vibrational quantum number, with relaxation to lower vibrational levels occurring—if indeed it does occur—only after the rotational quantum number has become quite small. Although we have made no serious attempt to estimate the relaxation rates, we believe that these energy differences, together with the values of the Cohen rate listed in Table I, suggest that collisional deexcitation of this molecule at normal temperatures is likely to proceed rapidly until the vibrational quenching rate has become rather high. To be more specific, we believe that the results shown in Table I and Fig. 2 suggest that relaxation of the $\mathrm{HeHe}_\mu{}^+$ is unlikely to be inhibited by large momentum changes or by adiabatic effects until this molecule has reached a state with very low angular momentum and a vibrational quantum number no larger than $v=13$ or 14, where the vibrational quenching rate is already approximately $10^8\ \mathrm{sec}^{-1}$.

It still remains to demonstrate—or, more precisely, to argue—that all necessary relaxation of the $\mathrm{HeHe}_\mu{}^+$ occurs in a time sufficiently short. We believe that any attempt to apply usual theoretical methods of estimating relaxation rates would not be a useful exercise in the present instance because these methods are not known for their quantitative, predictive reliability.[20,21] But if, simply for the purpose of discussion, the total collision cross section of $\mathrm{HeHe}_\mu{}^+$ in helium gas is assumed to be $\pi(2\ \mathrm{a.u.})^2$, the collision rate at room temperature and at 600 torr is approximately $9\times10^8\ \mathrm{sec}^{-1}$. We suspect that $9\times10^8\ \mathrm{sec}^{-1}$ is a conservative estimate of the actual deexcitation rate in very high vibrational levels of $\mathrm{HeHe}_\mu{}^+$, since the values of $R_{\max}$ listed in Table I for the potential $V=V_M+V_{\mathrm{LR}}$ indicate a geometrical cross section larger than $\pi(2\ \mathrm{a.u.})^2$ and the energy differences shown in Fig. 2 suggest that there should be little inhibition of inelastic transitions due to large momentum changes or to adiabatic effects. It can also be added that even the comparatively large values of $R_{\max}$ listed in Table I for very high vibrational levels might, by themselves, imply unrealistically low cross sections in some instances since the long-range ion-induced dipole interaction seems likely to play a role in the deexcitation of such loosely bound states. It would therefore seem reasonable to expect that relaxation to a state in which the vibrational quenching rate is roughly $10^8\ \mathrm{sec}^{-1}$ or higher should occur in a time not longer than 10^{-8} sec. But in vibrational levels that are only moderately high, such as those with $5\le v\le 8$, the situation is likely to be very different. The results presented in Fig. 2 indicate that the vibrational spacings are considerably larger than thermal energies, thereby requiring relatively large translational momentum changes to accompany any further decrease in v, which would almost surely mean that the deexcitation rate would be far less than the very rough estimate ($9\times10^8\ \mathrm{sec}^{-1}$) quoted above for the collision rate. It therefore seems most likely that Cohen quenching in these levels—and probably even in slightly higher levels—would be much more probable than collisional deexcitation, especially at pressures well below 600 torr. In fact, we believe it would be awkward to argue otherwise. We also believe that the results shown in Table I and Fig. 2 suggest that vibrational quenching is most likely to occur in states with very low K and $8\le v\le 14$, with the lower values of v in this range being associated with the initial formation of the $\mathrm{HeHe}_\mu{}^+$ in a state with rather high rotational quantum number.

C. Additional remarks

Three items remain to be discussed. One is quenching in $\mathrm{He}_n\mathrm{He}_\mu{}^+$ molecules with $n\ge2$, and the other two are some further possible effects of the long-range force.

1. Quenching in complex ions

At pressures much higher than 600 torr there is good reason to believe that reaction (8), which is energetically favored[1,9] and which would proceed at a rate varying quadratically with the pressure (provided the pressure is not too high), might be much more likely to occur than Cohen quenching in $\mathrm{HeHe}_\mu{}^+$. In fact, the experimentally determined rate coefficient for reaction (9) reported in Ref. 16 implies that this is indeed what would occur. Once a triatomic molecule is formed, there is again a competition between collisional deexcitation, the various quenching processes, and (perhaps) the formation of even more complex structures. But collisional deexcitation can reasonably be expected to be more effective for $\mathrm{He}_2\mathrm{He}_\mu{}^+$ than for $\mathrm{HeHe}_\mu{}^+$, not only because $\mathrm{He}_2\mathrm{He}_\mu{}^+$ has smaller energy spacings and a larger geometrical cross section but also because the binary collision rate is higher at pressures favorable for triatomic molecule formation. These considerations, together with the estimate obtained in Sec. II for the Burbidge—de Borde rate in the lowest level of the triatomic molecule—which, relative to the Cohen rate, is even higher than in the diatomic molecule—suggest that the Cohen mechanism in $\mathrm{He}_2\mathrm{He}_\mu{}^+$ is likely to be the dominant quenching process in a more limited range of vibrational levels than in $\mathrm{HeHe}_\mu{}^+$. Of course, similar arguments also apply, probably even more strongly, to any symmetrically structured $\mathrm{He}_n\mathrm{He}_\mu{}^+$ molecules with $n\ge3$, for which, as argued in the Appendix, Ruderman quenching is likely also to be important in low vibrational levels. Therefore we believe that the nature of the $2s$ quenching recently observed at high pressures by Eckhause *et al.*[5] can be regarded as an open question.

2. Long-range force

The long-range term in the He-$\mathrm{He}_\mu{}^+$ interaction lowers the centrifugal barrier. This should increase the amount of collisional quenching, which is known to be due almost entirely to close collisions.[7,27] (For the purposes of the present discussion, we shall define a close collision as one in which the classical turning point is smaller than the separation at which the centrifugal barrier has its maximum.) The fraction of pairs of He and $He_\mu{}^+$ atoms with a given relative orbital angular momentum l having energy of relative motion greater than the height B_l of the centrifugal barrier at temperature T is

$$F_l = 1 - \mathrm{erf}[(B_l/kT)^{1/2}] \ . \qquad (13)$$

Figure 3 shows values of F_l at $T=300$ K for the two assumed forms of the molecular potential specified in Sec. III B. These values of F_l are plotted with respect to $l(l+1)$. To the extent that classical mechanics is valid, the relative numbers of close collisions for these two potentials are very nearly proportional to the areas lying beneath the two sets of points shown in Fig. 3. Therefore, to a very rough approximation, the long-range interaction should cause collisional quenching to be increased by an amount proportional to the relative difference between these two areas, which is not negligible. The preceding argument is, of course, a considerable simplification, not only because quantum-mechanical effects such as orbiting resonances are unlikely to be totally insignificant, but also because, for a given energy of relative motion, the amount of collisional quenching should decrease with increasing angular momentum since the distance of closest approach, even for so-called close collisions, necessarily becomes larger, which causes the maximum electric field experienced by the $He_\mu{}^+(2s)$ atom to decrease. Nevertheless, we suspect this may account in part for some of the discrepancies between the estimates of collisional quenching by Cohen and Bardsley[7] and those of an earlier calculation by Mueller *et al.*[27] in which long range forces were specifically neglected.

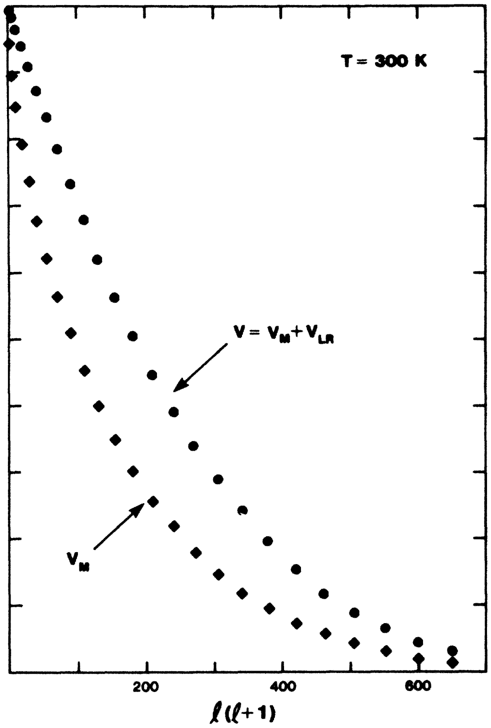

FIG. 3. The fraction F_l of pairs of He and $He_\mu{}^+$ atoms with relative orbital angular momentum l having energy of relative motion greater than the height B_l of the centrifugal barrier at temperature $T=300$ K. Results are plotted with respect to $l(l+1)$ for two assumed forms of the molecular potential, V_M and $V=V_M+V_{\mathrm{LR}}$, where V_M is a Morse potential and V_{LR} is a correction taking into account the long-range ion-induced dipole interaction.

Conceivably, the long-range interaction might also cause many-body effects to play a significant role in the occurrence of chemical reactions at high pressures. This could not only influence the production of diatomic and triatomic ions, which are believed to be usually formed in the relatively simple three-body association reactions (6) and (8), but it could also affect—perhaps even enhance—production of any $He_nHe_\mu{}^+$ molecules with $n \geq 3$. The ranges of internuclear separations for which production of $HeHe_\mu{}^+$ and $He_2He_\mu{}^+$ molecules should be due only to three-body collisions are not precisely known. But the calculations reported in Ref. 17 show that at room temperature roughly 20% of the $He_2{}^+$ molecules produced in reaction (7) are associated with classical trajectories for which, during the entire course of a three-body collision, the smallest value ever attained by the second largest of the momentary internuclear separations always exceeds 9 a.u. Moreover, even this relatively large distance is probably a conservative estimate of the maximum relevant separation for reaction (7) because, though it was not reported in Ref. 17, a detailed inspection of some of the trajectories computed in that investigation revealed that crossings of the so-called Wigner-Keck surface, which must occur an odd number of times during the course of a three-body collision if a diatomic molecule is to be formed, are frequently associated with at least one separation larger than 15 a.u. Although a separation this large probably presents no serious complication at 600 torr, where each helium atom can be thought of as occupying, on average, a volume equal to that of a cube of length 70 a.u., many-body effects would seem likely to be significant at pressures 2 orders of magnitude higher.

APPENDIX: RUDERMAN QUENCHING

The rate of Ruderman quenching will be denoted by γ_R. It is given by $\gamma_R = f\gamma_0$, where f is the amount of $2s \rightarrow 2p$ mixing in the $He_\mu{}^+$ atom due to electron excitation and $\gamma_0 = 2.0\times10^{12}$ sec^{-1} is the $2p \rightarrow 1s$ radiative rate. Estimates of γ_R are obtained below for a special model. This model is based on a $He_\mu{}^+(2s)$ atom held a fixed distance from a single, initially undistorted helium atom, with the perturbing interaction assumed to consist only of those components of the actual electrostatic interaction between the two that lead to first-order $2s \rightarrow 2p$ muon transitions. The mixing fraction f is estimated using two somewhat different methods. In one instance, it is estimated by employing an approximation to first-order perturbation theory that should be more or less reliable if the internuclear separation is sufficiently large, with the results then being applied to (possibly nonexistent) symmetrically structured $He_nHe_\mu{}^+$ molecules with $n \geq 3$. In the other instance, it is estimated for zero internuclear separation by employing a method used by Ruderman, with arguments then being given that the result probably represents a reasonably reliable upper limit to the mixing in a low level of $\mathrm{HeHe}_{\mu}{}^{+}$.

1. Description of model

If both the muonic atom and the helium atom are assumed to be initially undistorted, the unperturbed Hamiltonian is given in atomic units with sufficient accuracy by

$$H_0=-[1/(2m_\mu)]\nabla_\mu^2-2/r_\mu-\tfrac{1}{2}\nabla_a^2-2/r_a$$
$$-\tfrac{1}{2}\nabla_b^2-2/r_b+1/|\mathbf{r}_a-\mathbf{r}_b| \;, \tag{A1}$$

where m_μ is the reduced mass of the muon, $\mathbf{r}_\mu$ is the position of the muon with respect to the nucleus of the muonic atom, and $\mathbf{r}_a$ and $\mathbf{r}_b$ are the positions of the electrons with respect to the nucleus of the helium atom. The probable effect on the determination of f caused by neglecting the initial distortion of the helium atom, admittedly a questionable approximation, is discussed briefly at the very end of this appendix. As noted by Ruderman,[8] using an unperturbed Hamiltonian that does not take into account the $2s$-$2p$ splitting in the muonic atom should be an acceptable approximation because this splitting is small compared to the excitation energies of the electrons. The total electrostatic interaction between the two atoms is given with sufficient accuracy by

$$H_0'=H_a'+H_b' \;, \tag{A2a}$$

$$H_a'=2/R-2/|\mathbf{R}+\mathbf{r}_a|-1/|\mathbf{r}_\mu-\mathbf{R}|$$
$$+1/|\mathbf{r}_\mu-\mathbf{R}-\mathbf{r}_a| \;, \tag{A2b}$$

where $\mathbf{R}$ is the position of the nucleus of the helium atom with respect to the nucleus of the muonic atom. The definition of H_b' is similar to that of H_a'.

Since f is known to be small in isolated muonic atoms, it should suffice (i) to consider only the interaction H_a', (ii) to calculate an approximate solution of the equation

$$(H_0+H_a')\Psi=E\Psi \tag{A3}$$

using perturbation theory, and (iii) to multiply the amount of $2s\rightarrow 2p$ mixing thus obtained by a factor of 2. We shall, therefore, explicitly consider only one electron, whose position will henceforth be denoted by $\mathbf{r}_e$ rather than $\mathbf{r}_a$. The model that will be used to estimate f involves replacing both H_0 and H_a' in Eq. (A3) with other more or less equivalent expressions. The expression replacing H_0 explicitly involves only one electron but takes into account possible screening effects due to the other. The wave functions for the electron undergoing excitation will be approximated with hydrogenic functions. But because of the actual presence of another electron, we shall take into account the possibility that the most appropriate values of the effective nuclear charges for admixtures of excited electronic states could be different from that for the ground state. Accordingly, we shall replace the unperturbed Hamiltonian H_0 by

$$H=\sum_{l=0}^{\infty}H^{(l)}p^{(l)} \;, \tag{A4a}$$

where $H^{(l)}$ is defined by

$$H^{(l)}=-[1/(2m_\mu)]\nabla_\mu^2-2/r_\mu-\tfrac{1}{2}\nabla_e^2-Z_l/r_e \;, \tag{A4b}$$

and $p^{(l)}$, which is a projection operator acting on the angular part of the electron wave function, is defined by

$$p^{(l)}Y_{l',m}(\hat{\mathbf{r}}_e)=\delta_{l,l'}Y_{l',m}(\hat{\mathbf{r}}_e) \;. \tag{A4c}$$

The Hamiltonian H specified by Eq. (A4) allows the effective nuclear charge Z_l to depend on the orbital angular momentum l of the electron.[28] The second distinguishing feature of our model is that it involves retaining only those components of H_a' which lead to nonvanishing $2s\rightarrow 2p$ muonic matrix elements. These components of H_a' can be expanded in powers of $1/R$. It is convenient to write this expansion in the form

$$H'=\sum_{l=1}^{\infty}H_l' \;, \tag{A5}$$

where l is the multipole order of the dependence on $\hat{\mathbf{r}}_e$. Each term in Eq. (A5) is itself an expansion in powers of $1/R$. The calculations described below are concerned with finding an approximate solution of the equation

$$(H+H')\Psi=E\Psi \;. \tag{A6}$$

2. Estimate of f for large separations

Because the unperturbed electron is in the $1s$ state, each term H_l' in Eq. (A5) introduces an admixture of muon $2p$ states accompanied by admixtures of electron states with orbital angular momentum l. As noted by Ruderman,[8] admixtures of higher muon p states should be of negligible importance because relatively large energy differences would be involved. An approximate solution of Eq. (A6) can be written in the form

$$\Psi=\varphi_0+\sum_{l=1}^{\infty}\sum_{m=-1}^{1}\psi_{l,m} \;, \tag{A7a}$$

where the subscripts refer to the electron quantum numbers alone. The function φ_0 is the normalized eigenfunction of H for the unperturbed state, and the function $\psi_{l,m}$ is defined by

$$\psi_{l,m}=\sum_i\left[\int\varphi_{ilm}^{*}\Psi\,d\tau_\mu d\tau_e\right]\varphi_{ilm} \;, \tag{A7b}$$

where φ_{ilm} is the normalized eigenfunction of H for a state in which the muon is in the $2p$ state with magnetic quantum number $-m$ and the electron is in a state with orbital angular momentum l and magnetic quantum number m. The sum in Eq. (A7b) extends over all possible electron energies. It is convenient to write $\psi_{l,m}$ in the form

$$\psi_{l,m}=R_{21}(r_\mu)Y_{1,-m}(\hat{\mathbf{r}}_\mu)[u_{l,m}(r_e)/r_e]Y_{l,m}(\hat{\mathbf{r}}_e) \;, \tag{A8}$$

where R_{21} is the normalized radial wave function for a $2p$ muon. The total amount of $2s\rightarrow 2p$ muon mixing is given by

$$f=\sum_{l=1}^{\infty}f_l \;, \tag{A9a}$$

where

$$f_l=2\sum_{m=-1}^{1}\int_0^\infty [u_{l,m}(r_e)]^2 dr_e \ . \tag{A9b}$$

If the calculation is carried only to first order in H', the function $u_{l,m}$ is easily shown to be given approximately by the particular solution of the inhomogeneous differential equation

$$[-\tfrac{1}{2}d^2/dr_e^2+l(l+1)/(2r_e^2)-Z_l/r_e+Z_0^2/2]u_{l,m}(r_e) \\ =-2(Z_0)^{3/2}r_e\exp(-Z_0 r_e)g_{l,m}(r_e,R) \tag{A10}$$

that vanishes at $r_e=0$ and also as $r_e\to\infty$. The function $g_{l,m}$ appearing in Eq. (A10) is defined by

$$g_{l,m}(r_e,R)=(4\pi)^{-1}\int R_{21}(r_\mu)R_{20}(r_\mu)Y_{1,-m}^*(\hat{\mathbf{r}}_\mu) \\ \times Y_{l,m}^*(\hat{\mathbf{r}}_e)H_l' d\tau_\mu d\Omega_e \ . \tag{A11}$$

To order $1/R^5$, the functions $g_{l,m}$ obtained from the first three terms in Eq. (A5) are

$$g_{1,0}=(\sqrt{3}/m_\mu)(r_e/R^3) \\ \times[1-125/(8m_\mu^2R^2)-\tfrac{5}{4}(r_e^2/R^2)+O(1/R^4)] \ , \tag{A12a}$$

$$g_{1,\pm1}=[\sqrt{3}/(2m_\mu)](r_e/R^3) \\ \times[1-125/(4m_\mu^2R^2) \\ -\tfrac{5}{2}(r_e^2/R^2)+O(1/R^4)] \ , \tag{A12b}$$

$$g_{2,0}=-[9/(2\sqrt{5}m_\mu)](r_e^2/R^4)[1+O(1/R^2)] \ , \tag{A12c}$$

$$g_{2,\pm1}=-[3\sqrt{3/5}/(2m_\mu)](r_e^2/R^4)[(1+O(1/R^2)] \ , \tag{A12d}$$

$$g_{3,0}=[6/(\sqrt{7}m_\mu)](r_e^3/R^5)[1+O(1/R^2)] \ , \tag{A12e}$$

$$g_{3,\pm1}=[3\sqrt{6/7}/(2m_\mu)](r_e^3/R^5)[1+O(1/R^2)] \ . \tag{A12f}$$

If the estimate of f is carried to arbitrary order in $1/R$, Eq. (A10) must be solved separately for each desired set of values of l, m, and R. However, if the series for the functions $g_{l,m}$ are carried only to lowest nonvanishing order in $1/R$, it is then possible to write

$$g_{l,m}(r_e,R)\simeq h_{l,m}(R)r_e^l \ , \tag{A13}$$

where the function $h_{l,m}$ has no dependence on r_e. It follows that an approximate solution of Eq. (A10) can be written as

$$u_{l,m}(r_e)\simeq h_{l,m}(R)v_l(r_e) \ , \tag{A14}$$

where v_l is the appropriate solution of the equation

$$[-\tfrac{1}{2}d^2/dr_e^2+l(l+1)/(2r_e^2) \\ -Z_l/r_e+Z_0^2/2]v_l(r_e) \\ =-2(Z_0)^{3/2}r_e^{l+1}\exp(-Z_0 r_e) \ . \tag{A15}$$

Equation (A15) depends on neither m nor R. The total amount of $2s\to2p$ mixing is given approximately by

$$f^{(0)}=\sum_{l=1}^{\infty} f_l^{(0)} \ , \tag{A16a}$$

where

$$f_l^{(0)}=2\left[\sum_{m=-1}^{1}[h_{l,m}(R)]^2\right]\int_0^\infty [v_l(r_e)]^2 dr_e \ . \tag{A16b}$$

3. Numerical results and interpretation

The curve shown in Fig. 4 is a rough estimate of γ_R as a function of the internuclear separation. It was obtained using the approximation

$$\gamma_R\simeq(f_1^{(0)}+f_2^{(0)}+f_3^{(0)})\gamma_0 \ , \tag{A17}$$

with the values of the effective nuclear charge Z_l assumed to be

$$Z_0=Z_1=Z_2=Z_3=1.69 \ . \tag{A18}$$

If these charges are instead assigned the probably more realistic values

$$Z_0=1.69 \text{ and } Z_1=Z_2=Z_3=1.00 \ , \tag{A19}$$

the estimated quenching rates obtained with Eq. (A17) are lower than those shown in Fig. 4, the relative decrease varying from 33% at $R=1.75$ a.u. to 47% at $R=7.0$ a.u.

Figure 4 also shows the value of γ_R at $R=0$ for our model, as computed using the rather accurate approximation derived by Ruderman for $2s\to2p$ mixing in an isolated atom.[8] If $R=0$, the interaction given approximately for finite R by the series specified by Eq. (A5) is defined exactly by the dipole terms in the usual multipole expansion of $|\mathbf{r}_\mu-\mathbf{r}_e|^{-1}$. Ruderman's approximation for $2s\to2p$ mixing, which was obtained using closure, is given in terms of the ground-state electron wave function. The quenching rate at $R=0$ in Fig. 4 was computed assuming

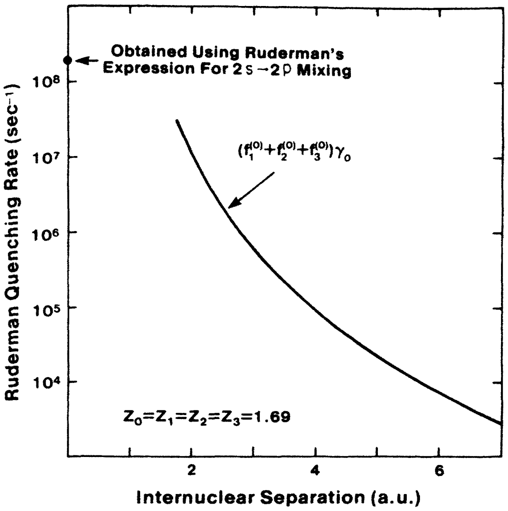

FIG. 4. Estimates of the rate of Ruderman quenching induced in a $\mathrm{He}_\mu{}^+(2s)$ atom by a single, initially undistorted helium atom.

that the ground-state wave function for the helium atom can be adequately approximated by $1s$ hydrogenic wave functions with effective nuclear charge $Z_0=1.69$ and that the effective nuclear charge experienced by the muon is $Z_\mu=2.0$. If the Ruderman rate for our model had been computed exactly for finite values of R, it would approach this value as $R\to 0$, no matter what values are assigned to the effective nuclear charges for the excited electrons.

The curve in Fig. 4 can be employed sensibly only if the internuclear separation is sufficiently large because each term in Eq. (A17) is proportional to a positive, even power of $1/R$. In the limit of very large R, only the first term, which is proportional to $1/R^6$, should be important, and the principal uncertainty in the value of γ_R should be due only to the value assigned to Z_1. However, at small separations the question arises as to whether or not the series is sufficiently convergent. Furthermore, there is another complication because the terms in Eq. (A17) are not all carried to the same order in $1/R$. Although this expression has the appearance of a truncated series, it is not a truncated series in powers of $1/R$ because even though the functions $g_{2,m}$ and $g_{3,m}$ used in computing $f_2^{(0)}$ and $f_3^{(0)}$ are all accurate to order $1/R^5$, the same is not true of the functions $g_{1,m}$, which were carried only to order $1/R^3$. If all terms of order $1/R^5$ are to be taken into account in the expansion of the perturbation, it is necessary to replace $f_1^{(0)}$ by

$$f_1^{(1)}=2\sum_{m=-1}^{1}\int_0^\infty [u_{1,m}^{(1)}(r_e)]^2 dr_e\ , \tag{A20}$$

where $u_{1,m}^{(1)}$ is the appropriate solution of Eq. (A10) for $l=1$, with the expression for $g_{1,m}$ carried to order $1/R^5$, as given in Eqs. (A12a) and (A12b). The function $u_{1,m}^{(1)}$ must be computed separately for each value of R.

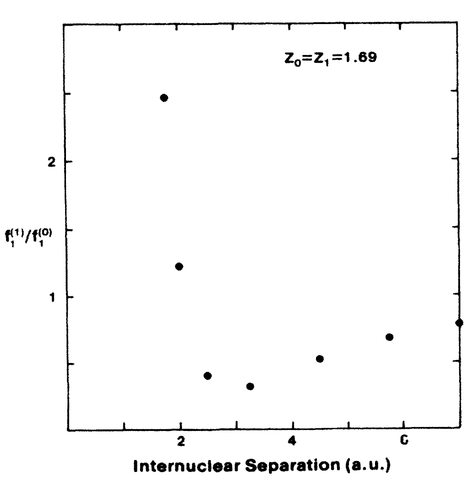

FIG. 5. The ratio $f_1^{(1)}/f_1^{(0)}$.

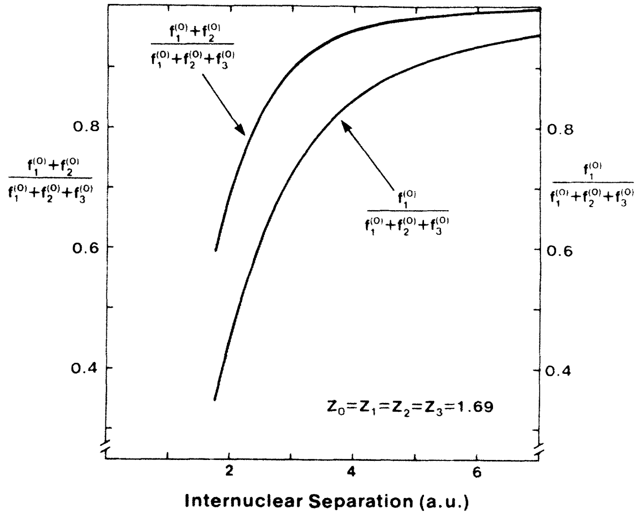

FIG. 6. Relative contributions of $f_1^{(0)}$ and $(f_1^{(0)}+f_2^{(0)})$ to the approximate expression $f\simeq(f_1^{(0)}+f_2^{(0)}+f_3^{(0)})$ for $2s\to 2p$ mixing in a $\mathrm{He}_\mu{}^+$ atom associated with electron excitation in a single, initially undistorted helium atom situated a fixed distance away. The scale is the same for both curves.

Figures 5 and 6 show some results that bear on the reliability of the curve in Fig. 4. Figure 5 shows values of $f_1^{(1)}/f_1^{(0)}$ for several values of R. Figure 6 shows the relative contributions of $f_1^{(0)}\gamma_0$ and $(f_1^{(0)}+f_2^{(0)})\gamma_0$ to the estimated rate given in Fig. 4. We believe that Figs. 5 and 6 together indicate that results obtained using Eq. (A17) for $R>2.0$ a.u. should be roughly equivalent to results obtained by retaining only the first three terms in Eq. (A5) and approximating each of them with a series to order $1/R^5$. Specifically, the relative error introduced into the curve in Fig. 4 by using $f_1^{(0)}$ instead of $f_1^{(1)}$ should range from a 10% underestimate at $R\simeq 2.0$ a.u. to as much as a 100% overestimate at $R\simeq 3.25$ a.u. We also believe that Figs. 5 and 6 together suggest that convergence of the entire series specified by Eq. (A9) should occur if $R>2.0$ a.u., with the underestimate introduced by taking into account only the first three terms being relatively modest, perhaps even as low as 20%. Furthermore, we tentatively conclude that these results, together with the value of γ_R at $R=0$ in Fig. 4 and the values of γ_R obtained using the effective nuclear charges specified by Eq. (A19), suggest that an estimated rate shown in Fig. 4 for $R>2.0$ a.u. is not likely to exceed by much more than a factor of 2 the exact rate for our admittedly not very realistic model based on a single, initially undistorted helium atom. But because no attempt was made to estimate corrections due to neglected terms in H' of order $1/R^6$ and $1/R^7$, this last assertion is, solely on the basis of our numerical results, perhaps a bit optimistic for separations between 2.0 and 3.0 a.u. However, some additional arguments supporting the use of Fig. 4 in more realistic situations are given below. For internuclear separations smaller than 2.0 a.u., there appear to be too many uncertainties to attempt any assessment of the accuracy of Eq. (A17), and we shall, therefore, not cite the curve in Fig. 4 in any discussion of Ruderman quenching in low levels of $\mathrm{HeHe}_\mu{}^+$ and $\mathrm{He_2He}_\mu{}^+$ molecules, which have He-$\mathrm{He}_\mu{}^+$ equilibrium separations of (very) roughly 1.45 and 1.75 a.u., respectively.[9,10] But we shall cite the relevant values of γ_R in Fig. 4 in discussing symmetric $\mathrm{He_3He}_\mu{}^+$ and $\mathrm{He_4He}_\mu{}^+$ ions, which (if they are in fact formed) should have He-$\mathrm{He}_\mu{}^+$ equilibrium separations of (very) roughly

2.1 and 2.4 a.u., respectively.[9] The values of γ_R in Fig. 4 for these two separations are approximately 8×10^6 sec^{-1} and 3×10^6 sec^{-1}. The larger of these numbers is equal to Cohen's estimate of the vibrational quenching rate in the lowest level of the triatomic ion, which he argued should be not too much larger than the rates in the lowest levels of any symmetrically structured $\mathrm{He}_n\mathrm{He}_\mu{}^+$ molecules with $n\geq3$ not considered in Ref. 9. In other words, we believe there is good reason to suspect that the Ruderman rate should be at least comparable to the Cohen rate in low vibrational levels of any of these relatively complex molecules.

Despite our reluctance to cite the curve in Fig. 4 in a discussion of low levels of diatomic and triatomic molecules, we harbor the belief that the value of γ_R shown at $R=0$ is probably a reasonably reliable upper limit to the Ruderman rate in the lowest level of $\mathrm{HeHe}_\mu{}^+$. This belief, which is cited in Sec. III A, is based partly on the nature of our model, and partly on the fact that Ruderman quenching and Burbidge–de Borde quenching have been estimated to be of comparable importance in the light elements if the K shell is filled.[8] With regard to the second of these two reasons, we note that the value of γ_R shown in Fig. 4 at $R=0$ is only slightly larger than our estimate of the Burbidge–de Borde rate in a low level of $\mathrm{HeHe}_\mu{}^+$, which is more or less consistent with the numerical results reported in Ref. 8.

Our estimates of the Ruderman rate given by the curve in Fig. 4 involve another approximation not taken into account by any of the results presented in Figs. 5 and 6. The interaction H_a' defined by Eq. (A2b) has components not included in the expansion specified by Eq. (A5). There are components of the total electrostatic interaction defined by Eq. (A2a) which are not responsible for any $2s\rightarrow2p$ muon transitions but which are responsible for a distortion of the helium atom. These components can be regarded as a neglected part of the unperturbed Hamiltonian. The neglect of the distortion of the helium atom is likely to be a significant source of error except at very large internuclear separations. We believe that this approximation tends to underestimate the actual Ruderman rate because the distortion should cause the amplitude of the initial electron wave function near the $\mathrm{He}_\mu{}^+$ atom to be larger than it is in our simple model. For this reason—and also because three or four helium atoms, not just one, are present in $\mathrm{He}_3\mathrm{He}_\mu{}^+$ and $\mathrm{He}_4\mathrm{He}_\mu{}^+$ molecules—we reaffirm our belief about the adequacy of the curve in Fig. 4 for separations greater than 2.0 a.u. The very brief mention of these relatively complex molecules in Sec. III C 1 involves implicitly the assumption that the appropriate values of the rate in Fig. 4 are unlikely to be larger than the actual Ruderman rate in low-lying levels by much more than a factor of 2 and that the actual Ruderman rate is, therefore, likely to be at least comparable to the Cohen rate. To a certain extent this is a guess, but it is a guess that we believe to be more or less reasonable and probably not much more daring than the extrapolation of the Cohen rate to more complex molecules suggested in Ref. 1 on the basis of results obtained for $\mathrm{HeHe}_\mu{}^+$ and $\mathrm{He}_2\mathrm{He}_\mu{}^+$. As with the Burbidge–de Borde rate, our estimates of the Ruderman rate should be directly applicable only to low vibrational levels, where the internuclear separations are restricted to relatively narrow ranges centered on the equilibrium values.

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