Radiative decay of the HeH$^+$($b\,^3\Sigma^+$) molecular ion

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The rate of the radiative decay of the HeH$^+$($b\,^3\Sigma^+$) molecular ion has been investigated. At infinite internuclear separation the $b\,^3\Sigma^+$ electronic state dissociates to form metastable atomic helium He($2\,^3S$) and a proton H$^+$. The optically allowed electronic transition to the lowest triplet HeH$^+$($a\,^3\Sigma^+$) state which dissociates to He$^+$($1s$) and H($1s$) was considered. This transition can lead to the population of metastable triplet ($a\,^3\Sigma^+$) states in beams of HeH$^+$ ions. [S1050-2947(96)05612-0]

I. INTRODUCTION

In a recent experimental study of the dissociative recombination (DR) of HeH$^+$ [1,2] it was proposed that metastable ions in the lowest electronic triplet state ($a\,^3\Sigma^+$) (which dissociates at internuclear separation $R\to\infty$ to He$^+$($1s$)+H($1s$), total spin $S=1$) may be responsible for the large cross sections observed. This ion can be produced in an ion source along with the ground-state molecular ion HeH$^+$($X^1\Sigma^+$) [which dissociates to He($1s^2$)+H$^+$ at $R\to\infty$]. The DR cross section for the metastable $a\,^3\Sigma^+$ ion should be very large due to the large number of suitable neutral states which cross its potential-energy curve [1]. The ground electronic state $X^1\Sigma^+$ does not have any suitable neutral state crossings and so the direct DR of an ion in this state will be slow [3]. Recent theoretical studies, however [4,5], involving indirect recombination via the repulsive neutral states of HeH have predicted sizeable cross sections (with rich resonant structures) for the DR of HeH$^+$.

The $a\,^3\Sigma^+$ electronic state has a very shallow potential well, $\sim$0.1 eV, at its equilibrium internuclear distance of $R\simeq4.4a_0$ and supports five vibrational levels for ^{4,3}HeH$^+$ and seven vibrational levels for ^{4,3}HeD$^+$ [1]. This ion can easily be destroyed by collisions in an ion source and so it is a problem to explain the population of such an excited state in the experiment [1].

In this paper it is proposed that the HeH$^+$($a\,^3\Sigma^+$) molecular ion can be created as a result of the optically allowed electronic dipole transition

$$\text{HeH}^+(b\,^3\Sigma,v_i)\to h\nu(\sim 8\ \text{eV})+\text{HeH}^+(a\,^3\Sigma,v_f) \quad \text{(A)}$$

$$\to \text{He}^+(1s)+\text{H}(1s)+h\nu \quad\quad \text{(B)}$$

from the second triplet excited molecular ion HeH$^+$($b\,^3\Sigma^+$) which dissociates to He($2\,^3S$)+H$^+$ at $R\to\infty$. Metastable triplet atomic helium He($2\,^3S$) is easily created in an ion source and so the molecular ion $b\,^3\Sigma^+$ must also be present. The HeH$^+$($b\,^3\Sigma^+$) ion potential well is deep enough, $\sim$0.7 eV [6], to survive against collisions. The process A can provide a substantial population of HeH$^+$($a\,^3\Sigma^+$) ions in the region downstream from the ion source exit canal in spite of collisions within the source that would otherwise destroy such ions. Process B is the radiative dissociation of the $b\,^3\Sigma^+$ state and this competes with process A.

The main problem investigated in the present paper is the ratio of the relative probabilities of channels A and B. This ratio depends on the relative positions of the potential wells belonging to the initial and final electronic states. The potential wells of the two states are shown in Figs. 1 and 2. The overlap integral between the wave functions of the ground vibrational levels of the two potential wells is very small,
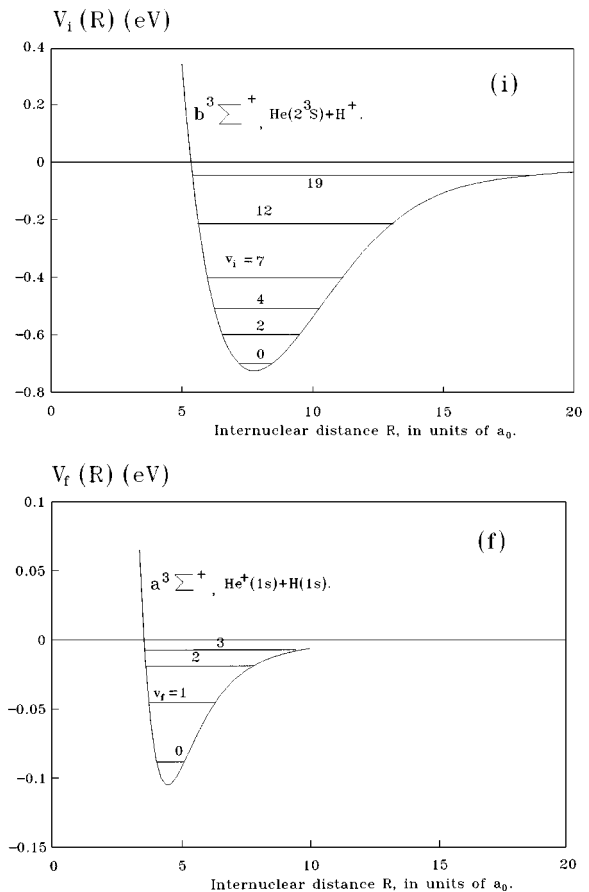

FIG. 1. Relative positions of the initial $b\,^3\Sigma^+$ (i) and final $a\,^3\Sigma^+$ (f) potential wells of the HeH$^+$ molecular ion.
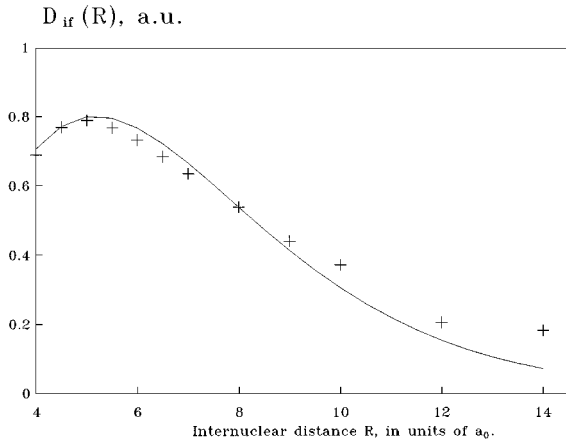
FIG. 2. Matrix element of the electronic dipole transition D_{if} (a.u.) as a function of the internuclear distance R. Crosses: numerical values [6], solid curve: analytical expression (11).

10^{-4}–10^{-5}, but for the first vibrationally excited levels, the overlaps are close to unity. Our present calculations show that a significant fraction of the radiative transitions proceed via the A route for the vibrational levels $v_{i,f}=0-3$.

An astrophysical review by Roberge and Dalgarno [8] lists many processes involving atomic H and He and molecular HeH and HeH$^+$. Collisional-radiative destruction of metastable atomic helium and radiative electron capture

$$\mathrm{He}(2\,^3S)+\mathrm{H}^+\rightarrow\mathrm{HeH}^+(a\,^3\Sigma^+,v_f)+h\nu \qquad (C)$$

$$\rightarrow\mathrm{He}^+(1s)+\mathrm{H}(1s)+h\nu \qquad (D)$$
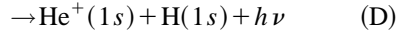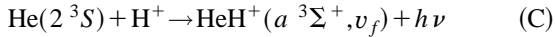
should be added to these processes. In processes C and D, the initial electronic state is the same as that in processes A and B but in C and D the atomic helium and hydrogen are initially in the vibrational continuum belonging to the initial electronic $b\,^3\Sigma^+$ state. In process C, the HeH$^+$($a\,^3\Sigma^+$) molecular ion is also formed as in process A.

II. RADIATIVE LIFETIME OF THE HeH$^+$($b\,^3\Sigma^+$) MOLECULAR ION

A. General

The probability per unit time of a radiative decay W_{if} after summation over the photon polarization is equal to

$$W_{if}=\frac{4}{3}\frac{e^2\omega^3}{\hbar c^3}|\langle i|\vec{r}|f\rangle|^2, \qquad (1)$$

where c is the velocity of light and the matrix element of the dipole transition is equal to

$$\langle i|\vec{r}|f\rangle=\langle\chi_f^*(\vec{R})\psi_f^*(\vec{R},\vec{r})|\vec{r}|\chi_i(\vec{R})\psi_i(\vec{R},\vec{r})\rangle, \qquad (2)$$

where $\vec{R}$ is the internuclear separation vector, χ is the wave function of the nuclear motion, ψ is the wave function of the two electrons in the HeH$^+$ ion. The coordinate system origin is placed at the molecular center of mass.

The vector of the electronic matrix element $\vec{D}_{if}(\vec{R})$ is directed along the vector of the internuclear separation $\vec{R}$

$$\vec{D}_{if}(\vec{R})=\frac{\vec{R}}{R}D_{if}(R) \qquad (3)$$

and the absolute value of the electronic matrix element

$$D_{if}(R)=\langle\psi_f^*(R,\vec{r})|\vec{r}|\psi_i(R,\vec{r})\rangle \qquad (4)$$

has been calculated numerically by Michels [6] as a function of the internuclear separation R.

Using standard techniques for the summation over the final molecular rotational states K_f and averaging over the molecular initial K_i states we can write for dipole transitions

$$W_{if}=\frac{4e^2\omega^3/9\hbar c^3}{2K_i+1}[(K_i+1)|\langle\chi_{K_i}^i(R)|D_{if}(R)|\chi_{K_i+1}^f(R)\rangle|^2$$
$$+K_i|\langle\chi_{K_i}^i(R)|D_{if}(R)|\chi_{K_i-1}^f(R)\rangle|^2], \qquad (5)$$

where the wave functions of the intramolecular motion χ are solutions of the following wave equations:

$$\frac{d^2\chi^{i,f}}{dR^2}+\frac{2M}{\hbar^2}\left[E_{v_{i,f}}-V_{i,f}(R)-\frac{K(K+1)}{2MR^2}\right]\chi^{i,f}=0, \qquad (6)$$

where $V_{i,f}(R)$ are the potential energies of the interatomic interaction on the initial (i), $b\,^3\Sigma$ and the final (f), $a\,^3\Sigma$ terms. The asymptotic behaviors of these potentials are determined by the polarization interactions $-\alpha/2R^4$ of the He($2\,^3S$)+H$^+$ and He$^+$($1s$)+H($1s$) systems. These asymptotes were joined with numerical terms [6] at large internuclear distances R and as a result we obtained the following asymptotic expressions:

$$V_i(R)=-\frac{158}{(R-0.013\,098)^4}; \qquad R\geq R_i=20.0; \qquad (7)$$

$$V_f(R)=-\frac{2.25}{(R-0.196\,799)^4}; \qquad R\geq R_f=9.5. \qquad (8)$$

These expressions correspond to values $\alpha_{\mathrm{He}(2\,^3S)}=316a_0^3$ and $\alpha_{\mathrm{H}(1s)}=4.5a_0^3$ [10]. At internuclear distances $R\leq R_{i,f}$ the numerical terms [6] were used.

Wave functions χ_v for all vibrationally bound states were normalized to unity

$$\int_0^\infty|\chi_v(R)|^2dR=1 \qquad (9)$$

and for the process of radiative dissociation B, the wave function of outgoing atoms χ_{Ef}, $E_f>0$, was normalized to the δ-function of energy

$$\chi_{Ef}\rightarrow\frac{1}{\hbar}\left(\frac{2M}{\pi k}\right)^{1/2}\cos(kR+\delta); \qquad \hbar k=\sqrt{2ME_f}; \qquad R\rightarrow\infty. \qquad (10)$$

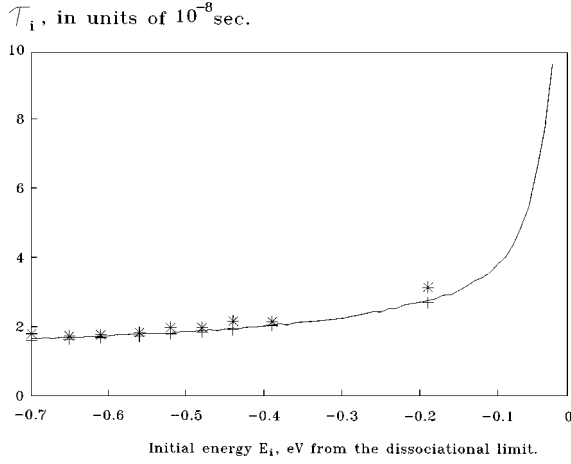In our calculations the next analytical expression for $D_{if}(R)$

FIG. 3. Total radiative lifetime of the HeH$^{+}(b\ ^{3}\Sigma^{+})$ molecular ion as a function of the initial vibrational energy E_i. Stars: results of quantum calculations using formula (5). Crosses: results using formula (16). Solid curve: result of the semiclassical approximation (19).

$$D_{if}(R) = A\left(1 - \frac{b}{\sqrt{R}}\right)R^{C}\exp(-dR) \qquad (11)$$

was used with numerical values $A = -0.8207$, $b = 1.320$, $C = 2.378$, and $d = 0.592$ in atomic units. Expression (11) corresponds to the asymptotic limit of D_{if} at $R \to \infty$ [9]. The values d and C are equal to $d = \sqrt{2J_{2\ ^3S}}$ and $C = 2/d - 1$, where $J_{2\ ^3S} = 4.7678$ eV $= 0.175\ 214$ a.u. is the ionizational potential of the atomic metastable triplet helium He($2\ ^3S$). The values A and b were chosen by fitting of expression (11) to the numerical D_{if} value [6] and the result of this fitting is shown in Fig. 3. This figure demonstrates the quality of the fit and the good agreement between both sets of data. For very large values of $R \geq 10a_0$, the asymptotic expression (11) should be better than the numerical values. The range of large $R \geq 10a_0$ is very important for calculations of the radiative lifetimes of high vibrational levels of HeH$^{+}(b\ ^{3}\Sigma^{+})$. These levels have greater radiative lifetimes than the ground vibrational level $v_i = 0$ and are especially interesting (see below).

Transition probabilities to the discrete vibrational states and to the vibrational continuum of the $a\ ^{3}\Sigma^{+}$ state have been calculated. The lifetime τ_i of the given initial state "i" is equal to

$$\tau_i = (W_i)^{-1}, \qquad (12)$$

where

$$W_i \equiv \left(\sum_{E_f} + \int dE_f\right)W_{if}(E_f) \qquad (13)$$

is the total radiative decay probability from the "i" state in the initial $b\ ^{3}\Sigma^{+}$ term to all the states to which the decay is possible: $\sum_{E_f}$ is the sum over the discrete vibrational states and $\int$ is the integral over the vibrational continuum of the $a\ ^{3}\Sigma^{+}$ term.

B. Total radiative lifetime

Let us consider the simplified method for calculating the total radiative lifetime. In accordance with the formulas (6),(13) we need to calculate the spectrum sum and integral

$$W_i \sim \left(\sum_{E_f} + \int dE_f\right)\omega_{fi}^3 |\langle\chi_i(E_i,R)|D_{if}(R)|\chi_f(E_f,R)\rangle|^2. \qquad (14)$$

We can remove the frequency of radiation $\omega_{fi} \equiv E_0 + E_i - E_f$ out of the $\Sigma, \int$ signs and use $\omega_{fi}^3 \cong |E_0 + E_i|^3$ because transitions with small E_f, $|E_f| \ll E_0$ or $|E_f| \ll |E_0 + E_i|$ ($E_{i,f}$ are measured from the dissociation limits), make the main contribution to the matrix element in Eq. (5). $E_0 = 0.32\ 477$ a.u. $= 8.8370$ eV is the energy difference between $a\ ^3\Sigma$ and $b\ ^3\Sigma$ states at $R = \infty$. Changing the order of the integration in the matrix element and the spectrum summation in Eq. (13) and using the completeness theorem

$$\left(\sum + \int dE_f\right)\chi(E_f,R)\chi(E_f,R') = \delta(R - R') \qquad (15)$$

we can rewrite expression (13) in the form

$$W_i \cong \frac{4}{9}\left(\frac{e^2\omega_0^3}{\hbar c^3}\right)\langle\chi_i(R)|D_{if}^2(R)|\chi_i(R)\rangle, \qquad (16)$$

where $\omega_0 \equiv E_0 + E_i$. Using also the normalized semiclassical wave functions χ_i for the molecular motion in the initial state

$$\chi_i^2(R) \cong 2\cos^2\left(\frac{1}{\hbar}\int_{R_1}^{R_2}p_i(R)dR - \frac{\pi}{4}\right) \Big/ v_i(R)\int_{R_1}^{R_2}\frac{dR'}{v_i(R')}, \qquad (17)$$

where $R_{1,2}$ are classical turning points and the classical velocity and impulse are equal to

$$v_i(R) = \sqrt{2[E_i - V_i(R) + K_i(K_i+1)/2MR^2]/M};$$

$$p_i(R) = Mv_i(R). \qquad (18)$$

Using the mean value $\cos(\ldots) \cong \frac{1}{2}$ we can rewrite the total radiation probability in the form

$$W_i \cong \frac{4}{9}\left(\frac{e^2\omega_0^3}{\hbar c^3}\right)\int_{R_1}^{R_2}D_{if}^2(R)\frac{dR}{v_i(R)} \Big/ \int_{R_1}^{R_2}\frac{dR}{v_i(R)}. \qquad (19)$$

Formula (19) is much simpler to use than the quantum calculation of the total radiative probability but at the same time it is sufficiently accurate (see below) (see Fig. 4).

C. Numerical calculations

Vibrational energy levels of the ^{4}HeH$^{+}(b\ ^{3}\Sigma^{+})$ molecular ion were calculated using two approaches; by a quantum-mechanical approach (for levels $v_i = 0 - 7,13$) and by a semiclassical approach (for all levels $v_i = 0 - 34$).

For the quantum-mechanical calculations a computer program was constructed which was used to solve the wave equation (6) for the initial $V_i(R)$ and the final $V_f(R)$ potentials and to calculate expression (5) (see Fig. 5). The interval
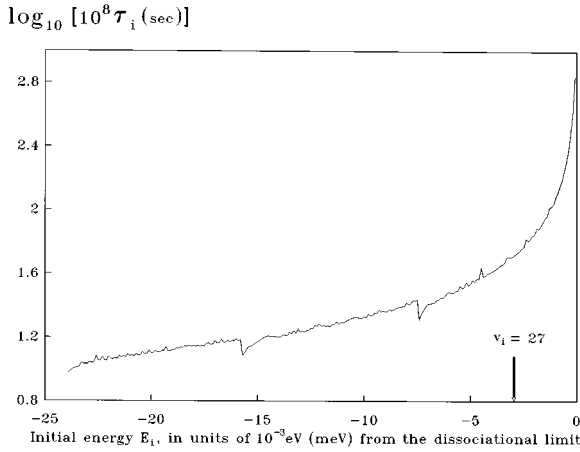
$\log_{10}[10^8\tau_i\,(\text{sec})]$

FIG. 4. Total radiative lifetime of the $\mathrm{HeH}^+(b\;^3\Sigma^+)$ molecular ion as a function of initial vibrational energy E_i for very high vibrational levels and very small binding energies, obtained by the semiclassical approximation (19).

of internuclear distances $2a_0 \leqslant R \leqslant 22a_0$ was divided into 2×10^4 points with a spacing $dR = 0.001a_0$. A large number of integration points (20 000) is required due to the highly oscillatory nature of the molecular wave functions χ. Numerical solutions of Eq. (6) were derived using the predictor-corrector or Numerov method. Tables of the functions $V_{i,f}(R)$ calculated in [6,7] and the asymptotic expressions (7),(8) were used together with a third-order interpolation procedure.

Eigenvalues E_{vi}, E_{vf} and eigenfunctions $\chi_{vi,f}(R)$ of discrete vibrational states were determined by the following scheme. Two solutions were obtained. The first one had the starting point at $R = 2a_0$ and the end point at R_{mid}. The second one had the start point at $R = 22a_0$ and the end point also at R_{mid}. Starting values (boundary conditions) at first fourth points (predictor-corrector scheme) were calculated by the semiclassical approach. Starting values of the first solution were positive while starting values of the second one
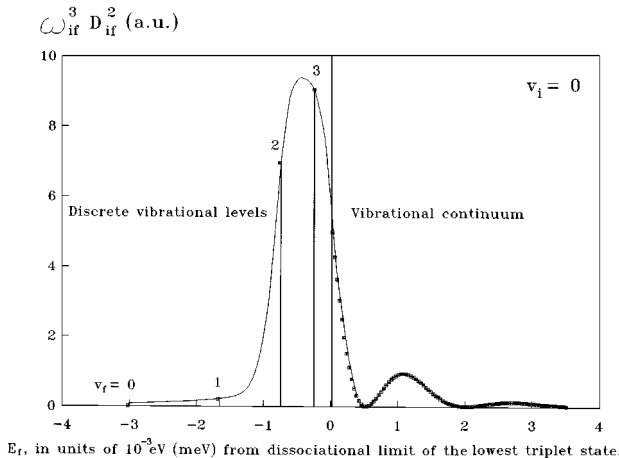
TABLE I. The vibrational energy levels E_{v_i} of $\mathrm{HeH}^+(b\;^3\Sigma^+)$, for $v_i = 0$ to 22, calculated using quantal and semiclassical approximations.

v_i	$E^q_{v_i}$ (eV)	$E^{sc}_{v_i}$ (eV)
0	-0.7005	-0.7005
1	-0.6529	-0.6533
2	-0.6071	-0.6072
3	-0.5622	-0.5623
4	-0.5186	-0.5184
5	-0.4757	-0.4757
6	-0.4342	-0.4344
7	-0.3943	-0.3945
8	—	-0.3559
9	—	-0.3184
10	—	-0.2824
11	—	-0.2484
12	—	-0.2164
13	-0.1861	-0.1861
14	—	-0.1577
15	—	-0.1316
16	—	-0.1079
17	—	-0.0867
18	—	-0.0685
19	—	-0.0533
20	—	-0.0413
21	—	-0.0313
22	—	-0.0232

were multiplied by $(-1)^v$. Both solutions were joined at a middle point R_{mid} and the relative difference of the derivatives was minimized to 10^{-4}–10^{-5} for all eigenvalues E_v.

Semiclassical wave functions in the vibrational continuum were used in parallel with numerical solutions. Results obtained by both wave functions agreed with high accuracy excluding the range of very small E_f values when the value of $\chi(R = 22a_0)$ was not asymptotical and the normalization procedure (10) could not be used for the numerical solution. The semiclassical result was used for these E_f values. An

$\omega^3_{if} D^2_{if}$ (a.u.)

FIG. 5. Radiative band of the HeH^+ molecular ion for the electron transition $b\;^3\Sigma^+ \rightarrow a\;^3\Sigma^+$ from the ground initial vibrational state $v_i = 0$. Points are results of quantum calculations using formulas (5). The line was drawn by hand.
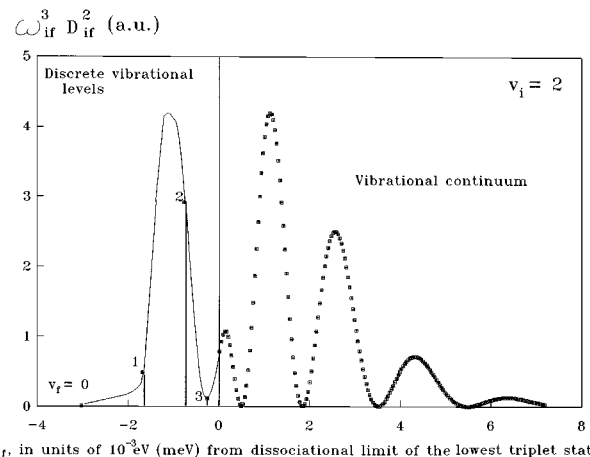
$\omega^3_{if} D^2_{if}$ (a.u.)

FIG. 6. The same as on Fig. 5 but for the initial vibrational state $v_i = 2$.

TABLE II. The vibrational energy levels E_{v_i} of HeH$^+$ ($b\ ^3\Sigma^+$) for $v_i = 23-34$. R_{outer} is the outer turning point of the nuclear motion (in atomic units); T is the period (in seconds) of the molecular motion. Numbers in square brackets indicate powers of 10.

v_i	$E^{sc}_{v_i}$ (eV)	$R_{outer}(a_0)$	T (sec)
23	-0.0167	23.1	2.2[-12]
24	-0.0117	25.2	2.8[-12]
25	$-0.007\ 91$	27.7	3.8[-12]
26	$-0.005\ 11$	30.9	5.3[-12]
27	$-0.003\ 12$	34.8	7.6[-12]
28	$-0.001\ 78$	40.1	1.2[-11]
29	$-0.000\ 92$	47.1	1.9[-11]
30	$-0.000\ 42$	57.1	3.4[-11]
31	$-0.000\ 16$	73.7	7.0[-11]
32	$-4.28[-5]$	102.4	2.0[-10]
33	$-6.12[-6]$	164.2	8.1[-10]
34	$-8.83[-8]$	482.0	1.93[-8]

uncertainty in the semiclassical wave function in the vicinity of the turning point was avoided by the use of the numerical solution of the wave equation (7) in the range around the turning point.

In semiclassical calculations of vibrational energy levels the relation

$$\int_{R_1}^{R_2} p(R)\,dR = \pi\hbar\left(v + \frac{1}{2}\right)$$

was used. Calculations were carried out up to very large distances ($482.0a_0$ for $v_i = 34$) and the outer turning points R_{outer} were determined as points where the difference $E - V(R)$ has changed its sign. The semiclassical values of the vibrational levels $E^{semcl}_{v_i}$, $0 \leq v \leq 34$, are given in Tables I and II.

For the total lifetime calculation we need to know the molecular spectral band $W_{if}(E_f)$ which should be an analytical function at any E_f value and in particular at the point $E_f = 0$. At this point, the discrete and continuum parts of the molecular spectral band are joined. Such a joining is shown in Fig. 6 for the state $v_i = 2$. In the discrete spectrum, the values $W_{if}(E_f)/[E(v_f + 1) - E(v_f)]$ are drawn, since for this joining the discrete spectrum values $W_{if}(E_f)$ should be multiplied by the number of states in the interval of the energy ΔE_f. From these figures it may be seen that a smooth joining takes place and that the molecular spectral band $W_{if}(E_f)$ is a very complicated function of the energy E_f. Smooth joinings of the continuum and discrete spectra for all other initial vibrational states considered (i.e., with $v_i > 2$) were derived and molecular spectral bands for large v_i are

TABLE III. Total number of vibrational levels in the He($2\ ^3S$)+H$^+$ potential well.

^{3}HeH$^+$	^{4}HeH$^+$	^{3}HeD$^+$	^{4}HeD$^+$
34	35	43	45

TABLE IV. The vibrational levels, E_{v_f} of the HeH$^+$($a\ ^3\Sigma^+$).

v_f	0	1	2	3
E_{v_f} (eV)	-0.0824	-0.0456	-0.0209	$-0.007\ 15$

much more complicated functions of E_i. Figure 6 demonstrates the good accuracy of our calculations.

III. RESULTS AND DISCUSSION

The HeH$^+$($b\ ^3\Sigma^+$) molecular ion is a very interesting species. Its potential well is shown in Fig. 1. It has a very broad well extending over the range $6 - 15a_0$. In spite of the relatively small dissociation energy, 0.7 eV, this well has 35 vibrational levels [for the ^{4}HeH$^+$($b\ ^3\Sigma^+$) isotope] which are shown in Tables I and II. Metastable atomic helium He($2\ ^3S$) has a huge polarizability, $\alpha = 316a_0^3$ [10] therefore the positions of the highest levels, $v_i = 20-34$, are determined by polarizational forces. The vibrational levels $v_i = 25-34$ have very small binding energies which are less then 0.01 eV: $E_{v_i=25} = -0.0079$ eV and $E_{v_i=34} = -8.8 \times 10^{-8}$ eV.[1] The molecular orbit sizes in these states are large: $R_{outer}(v_i=25) = 27.7a_0$ and $R_{outer}(v_i=34) = 482a_0$. Periods for the classical motion are shown in Table II and are large.

In Table III, total numbers of vibrational levels for the HeH$^+$ isotope molecular ions are shown. The heaviest ^{4}HeD$^+$ ion has the largest number of vibrational levels: $v_i^{max} = 45$.

In Table IV, new values of the vibrational energies E_{v_f} of the lowest triplet state HeH$^+$($a\ ^3\Sigma^+$) are shown and these are better, at the third decimal place than previous ones, [1] ($\delta E_{v_f} \sim 0.1\%$). However the Michels potential curves $V_{i,f}(R)$ [6] which were used by us have less accuracy than the Kolos potential curves [7]. At equilibrium distance $R = 4.5a_0$ the Kolos potential curve is $\sim 6\%$ deeper than that of Michels. At $R = 10a_0$ the difference between the two curves is equal to $\sim 1\%$. It means that correct values of $E_{0,1}$ are larger by $\sim 5\%$ than our values in Table IV. The difference $(E_1 - E_0)_{Kol}$ should be larger than $(E_1 - E_0)_{Mich}$ by about $1 - 2\%$ only.

Lifetimes for transitions between some individual discrete vibrational states $v_{i,f}$ are shown in Table V. For the transition between the vibrational states $v_i = 0 \rightarrow v_f = 0$ of the two electronic states, the lifetime is much greater than the total lifetime as a result of the small value ($\simeq 10^{-4}$) of the overlap integral of the vibrational wave functions for these states. For the first excited $v_{i,f}$ states, the lifetimes are close to the total ones and the overlaps of these states are close to unity.

Radiative transitions to the final $v_f = 4,5$ vibrational states are not presented in Table V though the semiclassical for-

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[1]The existence of the last vibrational level $v_i = 34$ is questionable because in the asymptotes (7),(8) higher-order momenta of the interaction should be taken into account. The correct values of the highest vibrational levels $v_i = 31-33$ also depend on the accuracy of the asymptotes (7),(8) but the existence of these levels is not questioned.

TABLE V. Radiative lifetimes for transitions from individual initial vibrational levels v_i of the He $(2\,^3S) + H^+$, $b\,^3\Sigma^+$ state to the individual final levels v_f of the He$^+(1S) + H(1s)$, $a\,^3\Sigma^+$ state. Numbers in square brackets indicate powers of 10.

	$v_i = 0$	$v_i = 1$	$v_i = 2$	$v_i = 3$	$v_i = 4$	$v_i = 5$
$v_f = 0$	1.03[−4]	3.28[−5]	1.49[−5]	8.47[−6]	5.59[−6]	3.87[−6]
$v_f = 1$	7.51[−7]	4.80[−7]	3.22[−7]	2.61[−7]	2.31[−7]	2.08[−7]
$v_f = 2$	3.94[−8]	1.10[−7]	9.45[−8]	1.72[−7]	2.26[−7]	3.98[−7]
$v_f = 3$	5.87[−8]	1.33[−7]	4.79[−6]	1.55[−7]	3.12[−6]	2.49[−7]

mula (19) takes into account transitions to all final states. The contributions of these states to the total lifetimes are small and do not exceed a few percent. The binding energies of these states are very small, see Table IV, and these states would be destroyed by collisions in an ion source and by the electric field in an accelerator as a result of electric-field predissociation [13].

Total lifetimes are shown in Table VI together with the ratios R_{vib} of the probabilities of the transitions to the discrete levels of the $a\,^3\Sigma^+$ state and to the vibrational continuum of this state. The total lifetimes have magnitudes of the order of 10^{-8} sec which are usual for optically allowed electronic transitions. The values of R_{vib}, the probability of reaction A in comparison with reaction B, are the main goal of our calculations. These values are not less than 10% even for $v_i = 13$, see Table VI.

In Figs. 4 and 5, the total lifetime is shown as function of the initial vibrational energy E_{v_i}. It can be seen that the total lifetime is increased by two orders of magnitudes when E_{v_i} approaches the vibrational continuum ($E_{v_i} \to 0$). This can be explained as follows: for high vibrational states the mean internuclear distance is large and the dipole momentum $D_{if} \to 0$ exponentially at $R \to \infty$, see Fig. 3 and formula (11). All three approaches, the quantum [formulas (5), (16)] and the semiclassical [formula (19)] give similar results, shown in Figs. 4 and 5.

The lifetime of metastable atomic helium He$(2\,^3S)$ is equal to 2 h and 12 min [14] so that the HeH$^+(b\,^3\Sigma^+)$ molecular ion can be formed generally speaking at any point inside an ion source. This fact, together with the quite large dissociative energy (0.7 eV) of the HeH$^+(b\,^3\Sigma^+)$ molecular ion and appreciable relative probability of reaction A, allows us to say that the radiative decay, considered above, may be a reasonable way of forming the HeH$^+(a\,^3\Sigma^+)$ molecular ion in an ion source. Obviously, in order to derive quantitative results, we need to know the populations of initial vibrational levels v_i and this information can be obtained by kinetic investigations.

All the results presented relate to a nonrotating HeH$^+(b\,^3\Sigma^+)$ molecular ion $K_i = 0$. From formula (5), in the dipole approximation, we can see that the rotational state of a final HeH$^+(a\,^3\Sigma^+)$ ion differs from an initial state by only ± 1, $K_f = K_i \pm 1$. If an initial molecular ion has a large K_i value then K_f is also large. The dissociation energy of the final state is small, 0.0824 eV (see Table IV), and for relatively small $K_f \sim 10$ the values of the initial vibrational levels are different from Table IV data. From the equality $K_f(K_f+1)/2MR_0^2 = 0.0824/27.21 = 0.003\,028$ we obtain (for the equilibrium distance $R_0 = 4.4a_0$) that at $K_f^{lim} \simeq 12$ the fi-

nal $a\,^3\Sigma^+$ state generally does not have stable vibrational levels. It means that, as a function of the rotational quantum number K, the probability of the creation of a vibrationally bound $a\,^3\Sigma^+$ state decreases at $K \geqslant 5$ and is equal to zero at $K \simeq 12$. [2]

At the same time the total radiative lifetime is not changed appreciably for these K values and is determined by transitions to the vibrational continuum of the final $a\,^3\Sigma^+$ term. Using formula (19) the calculation of the τ_i at $K_i = 15$ ($K_f = 14$ and 16) for the ground initial vibrational state $v_i = 0$ was performed. The value $\tau(v_i = 0) = 1.97 \times 10^{-8}$ sec has been derived and this value is close to the value 1.79×10^{-8} sec from Table V for $K_i = 0$.

Published papers about molecular radiative transitions are not numerous. We would like to note the papers [11,12] in which the radiative lifetime of the double charged HeH$^{2+}(2p\sigma)$ [dissociates $\to$ He^{2+} + H(1s)] molecular ion was investigated experimentally and theoretically. The electronic radiative transition HeH$^{2+}(2p\sigma) \to h\nu$ + He$^+(1s)$ + H$^+$ was considered. Like us, it was observed in these papers that the radiative lifetime is increased with the increase of the initial vibrational quantum number.

The HeH$^+(b\,^3\Sigma^+)$ molecular ions in the $v_i = 0-20$ states can act as an intermediate link for the formation of the weakly bound $a\,^3\Sigma^+$ ions that may have contributed to the experimental results in [1,2]. There is the possibility however, that the very high vibrational states $v_i > 27$ of this ion could have taken part directly in the DR process in these experiments since their lifetimes are comparable with the flight time from the ion source to the collision region. (Lifetimes of the $v_i < 27$ states are smaller than flight times). On the other hand, the binding energies of the $v_i > 28$ states are so small that they can easily be destroyed by collisions in the ion source and by electric field predissociation [13] in a Van de Graaff accelerator. Only the $v_i = 27$ and 28 states could have some chance to survive against collisions in the ion source and against the radiative decay during the flight from the ion source to the collision chamber and after this to take a part in the DR process directly. Quantitative conclusions about this must await additional calculation. [2]

The HeH$^+(b\,^3\Sigma^+)$ molecular ion can be formed in an ion source by three body collisions:

$$He(2\,^3S) + H^+ + X = HeH^+(b\,^3\Sigma^+) + X. \qquad (E)$$

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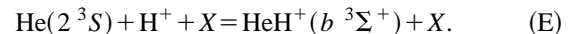
[2] For larger K values high vibrational levels exist and these levels are metastable due to the small probability of penetration through a rotational potential barrier.

TABLE VI. Total radiative lifetimes $\tau_{q,cl}$ of the individual initial vibrational levels v_i of the He(2 ^3S)+H$^+$, b $^3\Sigma^+$ state; τ_q is the total radiative lifetime determined by the summation over all transitions to the vibrational continuum and to discrete vibrational states v_f of the final a $^3\Sigma^+$ state; τ_{cl} is the total classical radiative lifetime [Eq. (13)]. R_{vib} is the relative contribution to the total radiative decay probability from transitions to the discrete vibrational states v_f only. Numbers in square brackets indicate powers of 10.

v_i	τ_q	τ_{cl}	R_{vib}
0	1.79[−8]	1.60[−8]	0.78
1	1.73[−8]	1.64[−8]	0.32
2	1.77[−8]	1.69[−8]	0.25
3	1.84[−8]	1.74[−8]	0.30
4	1.99[−8]	1.81[−8]	0.18
5	1.99[−8]	1.87[−8]	0.23
6	2.18[−8]	1.94[−8]	0.17
7	2.17[−8]	2.07[−8]	0.19
13	3.18[−8]	2.74[−8]	0.13

It is interesting to note that even an electron can act as a third body X for the formation of the HeH$^+$(b $^3\Sigma^+$) ion in $v_i=31-34$ vibrational states. At an electron energy $E_e\simeq0.05$ eV (temperature $T\simeq500$ K) the mean energy which can be transferred from an electron to the proton H$^+$ is equal to $m_e/M_{H^+}E_e\simeq2.7\times10^{-5}$ eV. This value is approximately equal to or greater than the energies of the $v_i=31-34$ vibrational states (see Table II).

Let us discuss now briefly the probability of the direct mechanism (C) for the formation of the HeH$^+$(a $^3\Sigma^+$) molecular ion. The cross section for process (C) can be written in the form

$$\sigma_C=\beta_{rad}\sigma_{dyn},\qquad(20)$$

where σ_{dyn} is the cross section for the approach of particles He(2 ^3S) and H$^+$ to a short distance [15]. β_{rad} is the radiative probability during this approach. For the polarization interaction, σ_{dyn} is equal to [15]

$$\sigma_{dyn}=\pi a_0^2\left(\frac{2\alpha}{E_C}\right)^{1/2},\qquad(21)$$

where $\alpha=316$ is the He(2 ^3S) polarizability, E_C is the collision energy in process (C). Expressions (20),(21) are used in the description of chemical ion-molecular reactions, (see, for example, [16]), and are correct for process (C) at the energies $E_C\leqslant1$ eV. The radiative probability β_{rad} can be written as the product: $\beta_{rad}=\beta_{rad}^0R_{vib}$, where β_{rad}^0 is equal to the ratio τ_{coll}/τ_{rad}. τ_{coll} is the mean time of duration of collision in reaction (C) and $\tau_{coll}\sim10a_0/v_{coll}(0.7$ eV$)$ $\sim4.6\times10^{-14}$ sec. According to Table VI, the total radiative lifetime $\tau_{rad}\simeq2\times10^{-8}$ sec and $R_{vib}\sim0.2$ and so $\beta_{rad}\sim4\times10^{-7}$. At the collision energy $E_C=0.05$ eV or 500 K, the dynamic cross section $\sigma_{dyn}=5.2\times10^{-14}$ cm^2 and for cross section (20) we obtain a value of $\sigma_C\sim2\times10^{-20}$ cm^2 [rate constant $\langle\sigma\times v_{coll}\rangle\sim6\times10^{-15}$ cm^3/sec]. It is most probable that this value overestimates the correct cross section σ_C. Process (C) should be investigated in detail in a separate paper.

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