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Molecule formation in tenuous media: Quantum effects in spontaneous radiative association*

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The semiclassical theory for the spontaneous radiative association coefficient is reviewed. The example of $H_2{}^+$ formation during a proton collision with a hydrogen atom is considered in both the Kramers and Ter Haar and the Bates versions of the semiclassical theory. These two semiclassical predictions are identical for $T > 50$°K. Below this temperature range they differ and show the small-T limiting behavior expected from asymptotic considerations. The quantum theoretical rate coefficient for the same process is also evaluated. For $500 \leq T \leq 32000$°K, the quantum and semiclassical rates are in quantitative agreement. The quantum rate and the Bates version of the semiclassical rate show identical temperature dependence as T becomes small, $O(T^0)$, but their magnitudes differ for $T \leq 500$°K. The quantum rate always exceeds the Bates semiclassical rate in this temperature range, with the maximum difference being nearly an order of magnitude. This enhancement of the rate of molecule formation due to quantum effects is anticipated to be important in the context of the interstellar media.

I. INTRODUCTION

The formation of molecules by spontaneous radiative association is usually dismissed as a mechanism important for the understanding of laboratory plasmas. The relatively long radiation time compared to the time the two heavy particles spend in close proximity, the collision time, is cited as justification, and the paucity of experimental radiative association data is consistent with this statement. These circumstances result in almost complete reliance on theoretical data when a study must include the radiation association mechanism.[1] For this reason, plus the fact that a clear understanding of any process is always important, the theoretical problem of radiative association is reconsidered in this paper.

The first quantitative formulation of the theory of radiative association and dissociation or, equivalently, opacity of diatomic molecules, was given by Kramers and Ter Haar.[2] They formulated the appropriate cross section by integrating the quantum radiation rate at a given internuclear distance R over a classical trajectory which is determined by the initial molecular interaction potential V_1, the collision energy, and an impact parameter b. The cross section is generated by integrating this result over all impact parameters. The cross section multiplied by collision velocity is averaged over the appropriate (Maxwellian) velocity distribution function to obtain the rate coefficient for molecule formation. This semiclassical treatment was reconsidered by Bates.[3,4] He pointed out that a naive interpretation of the Kramers–Ter Haar result would be incorrect for the case of a collision on an initial potential with an attractive, or bonding, region.

These semiclassical theories are considered in Sec. II, where special emphasis is placed on the low-temperature, T, behavior of the association rate coefficient. This temperature regime is especially important for the study of interstellar media where temperatures of the order of 10–20 °K are found.[5] The Kramers–Ter Haar rate diverges like $T^{-1/2}$ as $T \to 0$ for any attractive potential V_1. The low-temperature behavior including the Bates[3] correction term depends on the explicit long-range behavior of V_1, provided this behavior is also attractive.

Numerical data for both the Kramers–Ter Haar and the Bates semiclassical theories are also presented in Sec. II for the formation of $H_2{}^+$ by spontaneous radiation during collisions between H and H^+. These data repeat the results provided in Ref. 3 for $500 \leqslant T \leqslant 64000$ °K, and the agreement is excellent. The two versions of the semiclassical theory are identical in this temperature regime. Data for both versions of the semiclassical theory are also presented for $1.0 \leqslant T \leqslant 500$ °K. The ${}^2\Sigma_u^+(2p\sigma_u)$ state of $H_2{}^+$, which is the initial state for this case, does have an attractive region and is known to support a few discrete rotation-vibration (RV) states.[6] The Bates semiclassical rate thus differs from the Kramers–Ter Haar version for small T, and the numerical data presented for these two theories conform to the expected asymptotic behavior.

Section III considers the full quantum treatment of spontaneous radiative association. The only approximation involved in addition to the usual treatment of the radiation field is the distorted wave approximation. That is, the collision does not include coupling to other reaction channels. Consequently, unitarity is not guaranteed, but this is not thought to be an important restriction. The present approach is obviously based on the formalism of scattering theory. The relationship between reaction-rate theory and scattering theory for spontaneous radiative association has been discussed by Palmer.[7]

A quantum treatment of the frequency-dependent opacity of H_2^+, inversely related to the radiative association process, has been published.[8] The data presented in Ref. 8 are in substantial agreement with the corresponding semiclassical theory for the ranges of temperature and frequency considered. One reason for the differences between the two calculations was anticipated by Buchingham *et al.*[8] to be in part due to the truncation of the RV state manifold for the bound H_2^+. A recent treatment of this system[9] presents similar results. The RV manifold treated here is discussed in Sec. III and is thought to be exhaustive.

The data presented in Sec. III for H_2^+ formation will demonstrate some important quantum effects. The quantum and semiclassical theories are all in quantitative agreement for $T > 500\,^\circ\mathrm{K}$. This was to be expected because of the results available from Ref. 8, and this is also consistent with inferences based on the available quantum treatments of similar systems.[10, 11] The quantum rate coefficient exceeds the Bates semiclassical theory for $T < 500\,^\circ\mathrm{K}$. The maximum difference is nearly an order of magnitude and occurs for the smallest temperatures considered. Reasons for this enhancement of the quantum rate coefficient are discussed. The Bates semiclassical theory and the quantum theory are in qualitative agreement in that they both predict a constant rate as T becomes small. Some concluding remarks are given in Sec. IV.

II. SEMICLASSICAL THEORY

The semiclassical rate coefficient for molecule formation by spontaneous radiation during the collision of two atomic systems has been considered in some detail.[2, 3] These results will be briefly summarized and enlarged upon to facilitate the discussion of quantum effects. Formulas defining these theories and justifying the enlargements are not given because of space limitations.

The first semiclassical treatment of spontaneous radiative association was provided by Kramers and Ter Haar.[2] The radiation process was in fact treated quantum mechanically, and the term "semiclassical" refers only to the treatment of the collision mechanics. The colliding particles are assumed to follow classical trajectories, and their velocity distribution is assumed to be Maxwellian. The resulting rate coefficient will then depend only on the temperature defined by the Maxwellian velocity distribution and will be designated in the following by $\alpha(\mathrm{KT})$.

The $\alpha(\mathrm{KT})$ rate coefficient was shown by Bates[3] to be incorrect for the case of a collision on an initial molecular potential V_1 with long-range attractive character. This development was presented[3] for cases such that

$$\lim_{R\to\infty} V_1(R) = -\gamma R^{-\lambda}, \tag{1}$$

where R is the internuclear separation, γ is a positive constant, and $\lambda > 2$. Many important cases involving ground-state atomic species will be governed by Eq. (1) although, with slight modification, the Bates version should also be used for cases with V_1 having repulsive long-range behavior but which changes to bonding character for intermediate values of R. The Bates correction term is zero only for the case of a monotonically decreasing V_1 as R increases. The Bates rate coefficient is designated in the following discussion by $\alpha(B)$.

The asymptotic behavior of $\alpha(\mathrm{KT})$ and $\alpha(B)$ will clearly demonstrate the difference between these two theories. Bates[3] presents information in the spirit of approximate evaluations of $\alpha(B)$ that can be shown to be truly asymptotic in nature. Reasonable restrictions on the effective cross section for radiative association allow one to establish

$$\lim_{T\to\infty} \alpha(B) = O(T^{-3/2}), \tag{2}$$

a result implied by Eq. (37) of Ref. 3. Equation (2) will also apply to $\alpha(\mathrm{KT})$ and to the quantum rate coefficient, although the proof of Eq. (2) for these cases makes it clear that the magnitude of these rate coefficients need not be equal as T approaches infinity. Straightforward manipulations of the semiclassical rate coefficient can establish

$$\lim_{T\to 0} \alpha(\mathrm{KT}) = O(T^{-1/2}) \tag{3}$$

and

$$\lim_{T\to 0} \alpha(B) = O(T^{(\lambda-4)/2\lambda}). \tag{4}$$

Equations (26)–(36) of Ref. 3 imply the result given by Eq. (4).

The divergence of $\alpha(\mathrm{KT})$ in the limit of small T for all cases described by Eq. (1) and $\alpha(B)$ for

TABLE I. The spontaneous radiative association rate coefficients for H_2^+ formation during proton–hydrogen-atom collisions are given as a function of temperature. The semiclassical rates α(KT) and $\alpha(B)$ are defined in Sec. II. The data for the semiclassical rate α(Ref. 3) are from Ref. 3. The quantum rate $\alpha(Q)$ is defined in Sec. III. Temperature is in °K and the rate coefficient is in cm^3/sec.

T	α(KT)	$\alpha(B)$	α(Ref. 3)	$\alpha(Q)$
1.0	4.21 – 21	3.14 – 21		2.18 – 20
2.0	3.35 – 21	2.85 – 21		2.42 – 20
3.0	3.04 – 21	2.74 – 21		2.02 – 20
5.0	2.90 – 21	2.74 – 21		1.82 – 20
10.0	3.32 – 21	3.26 – 21		1.55 – 20
20.0	5.31 – 21	5.29 – 21		1.69 – 20
30.0	8.30 – 21	8.29 – 21		2.10 – 20
50.0	1.70 – 20	1.70 – 20		3.25 – 20
100.0		5.57 – 20		7.85 – 20
200.0		2.11 – 19		2.46 – 19
500.0		1.33 – 18	1.3 – 18	1.39 – 18
1000.0		5.27 – 18	5.2 – 18	
2000.0		1.93 – 17	1.9 – 17	
2500.0		2.86 – 17		2.88 – 17
4000.0		6.20 – 17	6.2 – 17	
8000.0		1.66 – 16	1.7 – 16	1.67 – 16
16 000.0		3.52 – 16	3.5 – 16	3.53 – 16
32 000.0		5.54 – 16	5.6 – 16	5.55 – 16
64 000.0		5.96 – 16	6.0 – 16	
100 000.0		5.05 – 16		
200 000.0		2.96 – 16		
500 000.0		1.04 – 16		

$2 < \lambda < 4$ may not be of particular significance since semiclassical theories become suspect in this limit. However, this does pose conceptual difficulties which can best be tested by comparison with quantum theory. Anticipating the results presented in Sec. III, Eq. (4) does appear to be correct for this H_2^+ case ($\lambda = 4$).

Reasons for the differences between $\alpha(B)$ and α(KT) are discussed in Ref. 3 and are paraphrased here in quantum language to facilitate subsequent discussion. When angular momentum is appropriately added to V_1, the resulting effective potential can have a maximum at some large R and a minimum for some smaller R. This condition will exist for a certain range of the angular-momentum quantum number J. The range of J is determined by the details of V_1. This angular-momentum barrier at large R results in the so-called three-turning-point problem for the collision wave function, provided the collision energy is sufficiently small, and the amplitude of the wave function is profoundly affected in the important bonding region of V_1. The construction of α(KT) implicitly ignores this angular-momentum barrier. In other words, complete penetrability of the angular-momentum barrier has been assumed. Bates,[3] in a manner consistent with classical trajectories, subtracts all contributions resulting from penetration of the angular-momentum barrier. The angular-momentum barrier is thus treated as if it were impenetrable in the derivation of $\alpha(B)$.

The preceding discussion of the semiclassical spontaneous radiative association rate coefficient is illustrated by the example of H_2^+ formation in a medium of H and H^+ having a Maxwellian velocity distribution. These data are provided in Table I and Fig. 1.

The V_1 for this case is the $^2\Sigma_u^+(2p\sigma_u)$ state of H_2^+. This state is usually said to be repulsive in character, but it does satisfy Eq. (1) with $\lambda = 4$. The maximum binding energy[12] is roughly 1.7 $\times 10^{-3}$ eV, and four discrete RV states are known to exist.[6] The asymptotic behavior required by Eqs. (2)–(4) is indicated by the labeling in Fig. 1. Of the two curves labeled "classical," the one with $O(T^{-1/2})$ behavior is the Kramers–Ter Haar rate and the one with $O(1)$ behavior results from the evaluation of Eq. (7) from Ref. 3. Table I presents selected data.

Bates[3] also evaluates $\alpha(B)$ for the case under consideration and for $500 \lesssim T \lesssim 64\,000$ °K. Some of the Ref. 3 data are repeated in Table I. The agreement is excellent and the very small differences can be attributed to the use of different data to describe the molecular potential curves and the electric-dipole transition matrix element. The values used here were taken from Refs. 12 and 13.

It should be emphasized that the example treated here cannot be expected to be typical of every system. The attractive character of V_1 is almost exclusively due to the long-range polarization force[6] and is very weak, as pointed out in a previous

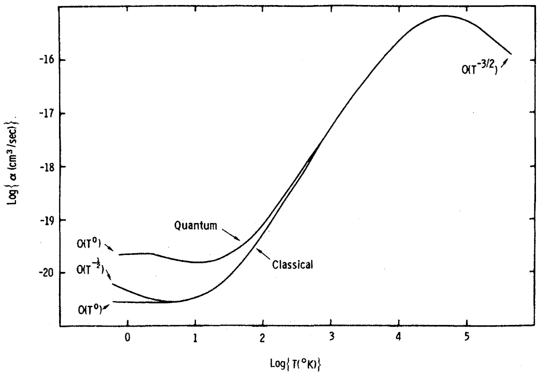

FIG. 1. The rate coefficients for the spontaneous radiative association of H and H^+ to form H_2^+ are shown as a function of temperature for the various theories discussed in the text.

paragraph. This weak bonding behavior accounts for the influence of the Bates correction term being limited to extremely low temperatures. If one equates Boltzmann's constant times T, kT, to the maximum possible quantum-mechanical angular-momentum barrier, 3.6×10^{-4} eV in this case, one finds $T\cong4\,^{\circ}\mathrm{K}$. This estimate represents a reasonable upper bound to the temperature for which $\alpha(B)$ and $\alpha(\mathrm{KT})$ display different dependence upon T and suggests that this method may provide a useful estimate in other cases. Since many systems, such as the astrophysically important CH molecule, have available V_1 curves with much stronger bonding character, the upper bound on T will occur for relatively larger T and, therefore, some care to include the Bates correction term should be exercised.

III. QUANTUM THEORY

The treatment of spontaneous radiative association presented in this section is typical of the many quantum calculations of similar radiative processes. The main difference is that here the interest is in the rate coefficient, while most investigations using quantum theory are usually concerned with frequency-dependent quantities. See Refs. 8 and 9 for applications to the frequency-dependent opacity of H_2^+ and Refs. 10 and 11 for studies of other molecular systems. Reference 14 and the citations therein present the quantum treatment of the rate coefficient which differs in detail from the following outline but they are, in principle, identical. Their results[14] are summarized in Sec. IV.

The possibility of events other than the radiative process under consideration are usually ignored.[8-11] This is termed the "distorted wave approximation." The initial eigenfunction is, accordingly, written as

$$\Psi_i(\vec{\tau},\vec{\mathrm{R}})=\psi_1(\vec{\tau},R)(4\pi)\times\sum_{lm}i^l\exp(-i\delta_l)Y_{lm}(\hat{R})Y^*_{lm}(\hat{q})X_l(R,q)\tag{5}$$

in the Born-Oppenheimer approximation for an electronic state with Σ symmetry. The final eigenfunction must be

$$\Psi_f=\psi_2(\vec{\tau},R)Y_{JM}(\hat{R})X_{vJ}(R)\,.\tag{6}$$

The symbol $\vec{\tau}$ represents the electronic degrees of freedom, including spin, and $\psi_n(\vec{\tau},R)$ is a molecular eigenfunction describing the electron motion when the nuclei of the colliding atoms are separated by a distance R. Discrete RV motion in the final electronic state, ψ_2, is represented by $Y_{JM}(\hat{R})X_{vJ}(R)$, where v, J, and M are the usual RV quantum numbers. The equations defining X_l and X_{vJ} are well known[15] and only require knowledge of the R-dependent electronic eigenenergies, V_1 and V_2, respectively.

The continuum motion of the colliding atoms is normalized, most conveniently for the present case, on the q scale to unit flux, where $\hbar q$ is the magnitude of the relative momentum of the colliding atoms. This requires

$$\int\int\int d\tau^3dR^3dq^3|\Psi_i|^2=8\pi^3\,.\tag{7}$$

Equation (7) is satisfied by Eq. (5), provided

$$\lim_{R\to\infty}X_l=(qR)^{-1}\sin(qR-\tfrac{1}{2}l\pi+\delta_l)\,,$$

and δ_l represents the phase shift. The remaining functions represent discrete motion and are thus normalized to unity in their respective spaces.

The wave functions and normalizations defined by Eqs. (5)–(7) are used to calculate the dipole transition matrix element. The substitution of this matrix element into the usual expression for the Einstein A coefficient results in a photon-emission rate coefficient differential in the space of $\vec{\mathrm{q}}$. Since the orientation of the collisions is presumed to be random and there is no differentiation with respect to the polarization of the emitted photon, we actually require

$$\sum_{vJM}\int d\Omega(\hat{q})\frac{d^3A}{dq^3}\equiv\frac{d\bar{A}}{q^2dq}=\frac{64\pi^2g}{3\hbar^4c^3}\sum_{vJ}g_J[\Delta E(vJ;q)]^3[(J+1)|D^{q\,;\,J+1}_{v\,;\,J}|^2+J\,|D^{q\,;\,J-1}_{v\,;\,J}|^2]\,.\tag{8}$$

The energy difference between the initial continuum state and final discrete state is indicated by $\Delta E(vJ;q)$ and, for the case of a $\Sigma\to\Sigma$ transition, the dipole matrix element is

$$D^{q\,;\,l}_{v\,;\,J}=\int dR\,\boldsymbol{R}^2X^*_{vJ}(R)\times\left(e\sum_j\int d\vec{\tau}\,\psi^*_2(\vec{\tau},R)Z_j\,\psi_1(\vec{\tau},R)\right)X_l(\boldsymbol{R},q)\,,\tag{9}$$

where Z_j is the coordinate of the jth electron along the unit vector $\hat{R}$. The sum over j includes all electrons making up the colliding system. Other symbols appearing in Eqs. (8) and (9) include the electronic statistical weight g, the rotational statistical weight g_J, the electron charge e, and Planck's constant divided by 2π, $\hbar$. Similar expressions replace Eqs. (5)–(9) if the symmetry of the electronic states is other than Σ in character.

The velocity distribution of the colliding atoms is presumed to correspond to thermodynamic equilibrium and is therefore described by some temperature T. Hence, the temperature-dependent quantum rate coefficient is defined by

$$\alpha(Q) = 2\pi(\pi kT)^{-3/2} \int dE\,\sqrt{E}\,\exp(-E/kT)\frac{d\bar{A}}{q^2 dq}, \tag{10}$$

where $\hbar^2 q^2 = 2\mu E$ and μ is the reduced mass of the colliding atoms.

Equation (10) has been evaluated for the H_2^+ case under consideration, and the results are given in Table I and shown in Fig. 1 as the quantum curve. It can be shown by standard methods that there are 423 discrete RV states in the $H_2^+\,{}^2\Sigma_g^+(1s\sigma_g)$ potential curve. In order to evaluate the sum over v and J, the matrix elements required by Eq. (8) were calculated for all values of v and every even value of J. The choice of q values was dictated by v and J and, basically, a logarithmic scale was used with sufficient points to guarantee reasonably accurate interpolation results to use in the evaluation of Eq. (10). The corresponding matrix elements for odd values of J were estimated by a cubic spline interpolation of available data for the matrix elements themselves rather than working with the square of the matrix elements. This J interpolation involves a rather strongly oscillating function and, therefore, the independent variable J was replaced by the cord length between adjacent matrix element values. This device has the effect of creating a smoother function for fitting with the cubic spline. The electronic matrix elements required by Eq. (9) were taken from Ref. 13, and the wave functions for nuclear motion were numerical functions generated by techniques described elsewhere.[15] Any error in the values of $\alpha(Q)$ presented in Table I is thought to be confined to the last quoted figure.

A study of the frequency-dependent opacity for this system[8,9] concluded that the semiclassical theory is not greatly different from the quantum theory. Similar conclusions have been reached in studies of other systems[10,11] and the numerical data presented here are consistent with these observations. As indicated by Table I and Fig. 1, the semiclassical and quantum theories for the rate of H_2^+ formation are in quantitative agreement for $T > 500\,°K$. The quantum result is always larger than the semiclassical, but by no more than 5%, in this range of T.

Rather large differences between the quantum and semiclassical theories are observed for $T < 500\,°K$. The quantum result exceeds the Bates semiclassical result by almost a factor of 10 in the limit of small T. This difference is due to a combination of two effects. First, there is the usual penetration of the $X_{vJ}(R)$ function beyond the right-hand turning point, which increases the value of Eq. (9) over that found if nuclear motion in the large-R forbidden region were ignored. Second, the weight given the formation of a particular RV state by the frequency factor $[\Delta E(vJ;R)]^3$ is a constant, while this factor is determined by the difference between the V_1 and V_2 potential curves for the semiclassical case (see Ref. 3). At large R this factor goes to zero in an exponential manner for the case under study and undoubtedly accounts in part for the extremely small semiclassical molecule-formation rate. Both factors are most important for the formation of RV states near the dissociation limit and, accordingly, quantum effects are most pronounced for small T. It is important to remember that the initial potential curve V_1 is essentially repulsive in the region of R where V_2 supports discrete RV states, hence for small collision momenta $\hbar q$ the formation of molecules will tend to produce RV states very near the dissociation limit.[3,4]

The quantum molecular-formation rate shows a hint of structure for $T < 10\,°K$. This is presumably due to the very few bound RV states entering into the sum required by Eq. (8) when $\hbar q$ becomes small. It is noteworthy that the extremely weakly bound $v = 19$, $J = 0$ state accounts for the major portion of $\alpha(Q)$ for $T \cong 1\,°K$; see the second article cited in Ref. 15.

The quantum rate was not calculated for $T > 32\,000\,°K$. At the highest T considered there were no obvious quantum effects attributable to penetration of nuclear motion into the forbidden region at small R in the V_2 potential. It is possible that a quantum enhancement of the formation rate will occur for $T > 32\,000\,°K$. However, there seems to be no reason to expect a large effect, since V_2 supports a large number of discrete RV states, and V_2 is rather steep in the small R region.

IV. SUMMARY

The asymptotic behavior of the semiclassical theory for spontaneous radiative association in the limit of low temperatures is reconsidered. The importance of the Bates correction term in this limit and the dependence of the association rate on the long-range nature of the interaction potential between the colliding atoms is emphasized. The specific case of H_2^+ formation during hydrogen-atom–proton collisions is recalculated for $500 \lesssim T \lesssim 32\,000\,°K$ and extended to the range $1 \leq T \leq 500\,°K$. The agreement with previously published data[3] is excellent. This particular case consists of a collision initially on the very weakly bound ${}^2\Sigma_u^+(2p\sigma_u)$ state of H_2^+ and, therefore, the Bates correction term must be nonzero. As a consequence of the weak bonding, however, the effect of the Bates correction term is shown to be important only for $T < 5\,°K$. This example demonstrates, for the first time, the small-T limit of the usual theory,[2] which diverges as $T^{-1/2}$, and the corrected theory,[3] which goes to a constant as $T \to 0$.

Bates[3] found semiclassical results for the radiative formation of CH and CH^+ which exhibited the temperature dependences required by Eq. (4) when $T \sim 100\,°K$. Results were not given[3] for the Kramers–Ter Haar semiclassical theory. Hence, the low-temperature behavior found here for application of the Bates semiclassical theory to the H_2^+ case was to be expected.

The quantum version of the spontaneous radiative association rate coefficient for this H_2^+ case is also presented for $1 \leq T \leq 32\,000\,°K$. The agreement with the semiclassical theories for $T > 500\,°K$ is remarkably good, being always larger, but by no more than 5%, in this temperature range. Considering the difficulty in completing the v, J sum required by Eq. (8), semiclassical rate coefficients are probably more reliable than are quantum rate coefficients for a restricted range of T. Quantitative estimates of this T range are hard to give in general, but any T that implies that the Eq. (8) v, J sum should contain more than 20 states seems to work for this case.

Quantum effects are quite apparent for $T < 500\,°K$. The maximum difference occurs for lowest temperature considered. Here the quantum theory exceeds the Bates semiclassical theory by nearly an order of magnitude (see Table I). The association rate coefficient for both the quantum and Bates semiclassical theories approaches some constant as $T \to 0$. Although the magnitudes predicted by the two theories are quite different, it is significant that there is agreement in their qualitative behavior for the example involving an ion-atom collision.

A recent quantum treatment[14] of the spontaneous radiative association rate coefficient for CH^+ and CH reaches quite different conclusions. Their quantum temperature dependence for small T is given as $O(T^{-1/2})$ for both systems, which is identical to the Kramers–Ter Haar semiclassical behavior [see Eq. (3)]. As pointed out in a preceding paragraph, Bates[3] found $O(T^0)$ and $O(T^{1/6})$ behavior for the CH^+ and CH cases, respectively. In addition, the magnitude for the quantum rate is less than that for Bates semiclassical rate[14] for $T \sim 100\,°K$.

One essential difference between the quantum treatments presented here and in Ref. 14 is that the effects of angular momentum on the vibrational wave functions were ignored in Ref. 14. Specifically, $X_l(R, q)$ of Eq. (5) and $X_{vJ}(R)$ of Eq. (6) were replaced by their rotationless counterparts. This approximation will obviously exclude from the quantum rate coefficient any effects that are due to angular-momentum barriers. Since the semiclassical theory of Kramers and Ter Haar contains a similar approximation (see the discussion in Sec. II and Ref. 3), it seems probable that the similarity in temperature dependence for small T is a consequence of neglecting angular-momentum effects. A proof that the full quantum rate coefficient should have the same low-temperature behavior as does the Bates semiclassical theory is not available but the present data do not yet appear to rule out this conclusion.

The magnitude comparisons between the quantum and semiclassical theories for the H_2^+ and the CH^+ and CH cases[14] also pose a problem. A rationalization for quantum results exceeding semiclassical results for H_2^+ when T is small was presented in Sec. III, and care to be exhaustive in the rotation-vibration sum required by Eq. (8) has long been recognized.[8] Reasons for the increasingly good agreement between quantum and semiclassical theories as T increases were not discussed in the context of the H_2^+ case presented here, but the general success of semiclassical arguments has long been recognized. Completeness in the sum over v and J for the H_2^+ case is implied by this type of agreement. Similar data are unfortunately not available[3,14] for the CH^+ and CH cases. These statements, however, do not prove that quantum rate coefficients should always exceed semiclassical rate coefficients in the low-temperature region, and generalities on this point must be avoided.

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