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AN UPDATE OF AND SUGGESTED INCREASE IN CALCULATED RADIATIVE ASSOCIATION RATE COEFFICIENTS

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ABSTRACT

A sizable number of radiative association reaction rate coefficients involving polyatomic molecular ions have now been calculated and utilized in ion-molecule models of the chemistry of dense interstellar clouds. Recent evidence suggests that these calculated rate coefficients may be an order of magnitude too low in many cases. The evidence is reviewed and developed and calculated rate coefficients are updated. In addition, the temperature dependence of each reaction rate coefficient in the 10–50 K range is estimated if this information has not previously appeared in the literature.

Subject heading: molecular processes

I. INTRODUCTION

Radiative association processes play an important role in the formation of complex interstellar molecules by gas phase ion-molecule reactions (e.g., Leung, Herbst, and Huebner 1984). Although some radiative association reactions have been studied in the laboratory (Barlow, Dunn, and Schauer 1984; Woodin and Beauchamp 1979; McEwan *et al.* 1980; Bass *et al.* 1981), most processes of interstellar importance must have their rates obtained by theoretical methods (Bates 1983*a*, *b*; Herbst 1980*a*, *b*). In all theoretical treatments, the radiative association process is assumed to proceed via an intermediate complex or unstable molecule which must be stabilized via emission of a photon before redissociation into reactants. A significant part of the theoretical treatment of radiative association processes is the determination of the radiative stabilization rate of the intermediate complex formed by the reactants. The complex can be stabilized by the emission of a single infrared photon during a transition between molecular vibrational levels so that the radiative stabilization rate can be equated to the rate of infrared vibrational emission of the molecule at an energy approximately equal to its bond energy. Woodin and Beauchamp (1979) and Herbst (1982*a*) have presented theories of vibrational infrared emission of polyatomic molecules and have determined rates of the order of 1.0(+2) s^{-1} for typical polyatomic molecules with several eV of excitation. This value or something close to it has been utilized in recent treatments of important interstellar radiative association processes which involve the synthesis of molecular ions (Leung, Herbst, and Huebner 1984, hereafter LHH; Bates 1983*a*, *b*). However, very recent experimental and theoretical evidence indicates that the vibrational emission rate of polyatomic molecular ions is an order of magnitude faster than previously assumed in these treatments. In this paper, the theoretical evidence for this assertion is explained and developed. The faster radiative stabilization rate is utilized to lessen the discrepancy between theory and experiment on the important interstellar association between CH_3^+ and H_2. Finally, proposed updated rate coefficients for a variety of radiative association processes in the temperature range 10–50 K are given for inclusion in future models of dense interstellar clouds.

II. RADIATIVE STABILIZATION RATES

In the theory of Herbst (1982*a*) which will be utilized here, the overall rate of spontaneous emission $A(s^{-1})$ of a polyatomic molecule undergoing vibration is given by the expression

$$A(E_{\rm vib}) = \sum_n P_n(E_{\rm vib}) \sum_m A_{n-m} , \qquad (1)$$

where $E_{\rm vib}$ is the vibrational energy of the molecule, P_n is the probability of observing the molecule to be in state n of a large number of states at energy $E_{\rm vib}$, and A_{n-m} is the Einstein A coefficient for spontaneous emission from state n to state m. The sum over m extends over all vibrational states connected to n by dipole selection rules whereas the sum over n extends over all states at energy $E_{\rm vib}$.

The spontaneous emission rates A_{n-m} are evaluated with the approximation that the molecule is "mechanically harmonic"; i.e., that the molecule can be regarded as a set of harmonic oscillator modes. The probabilities P_n are calculated via the statistical equal a priori hypothesis and the use of a density-of-states argument. The assumption of "mechanical harmonicity" allows the Einstein spontaneous emission rate coeffficient of a polyatomic molecule at energy $E_{\rm vib}$ to be expressed in terms of "fundamental" Einstein A coefficients for the various harmonic oscillator modes of the molecule. These coefficients, labelled $A_{1-0}{}^{(i)}$, $A_{2-0}{}^{(i)}$, and $A^{(i,j)}_{1,1-0,0}$, refer to the lowest normal, overtone, and combination transitions of the various harmonic oscillator modes. These coefficients can in turn be obtained from either experimental studies of infrared intensities or from quantum-mechanical calculations of these intensities. The additional assumption of "electrical harmonicity" in which the overtone and combination terms are ignored must often be made because of the paucity of experimental or theoretical data concerning these terms.

Herbst (1982*a*) utilized experimental and theoretical data concerning a variety of neutral polyatomic molecules to determine their spontaneous emission rates as a function of $E_{\rm vib}$ and found that at several eV of vibrational energy all of the neutral molecules studied possess spontaneous emission rates in the range 30–300 s^{-1}. He then asserted that most molecular ions are likely to possess similar rates, although there was little experimental or quantum chemical information available at the time concerning the infrared intensities of molecular ions. A theoretical paper on H_3^+ intensities (Carney and Porter 1976) did yield large infrared intensities, but it was felt that the lightness of this species made it unique.

Quite recently, two papers have appeared in the literature on the infrared intensities of polyatomic molecular ions. Colvin *et al.* (1983) have undertaken quantum chemical calculations on the ion H_3O^+, while Lee and Schaefer (1984) have undertaken quantum chemical calculations on the ion $HCNH^+$. Utilizing these intensities in the theory of Herbst (1982*a*) results in the spontaneous emission rates seen in Figure 1. The spontaneous emission rates of these two ions are quite high compared with all the neutral species previously studied by Herbst (1982*a*). At a vibrational energy of 3 eV, for example, the spontaneous emission rates of H_3O^+ and $HCNH^+$ are 2.3(+3) s^{-1} and 1.1(+3) s^{-1} respectively. That molecular ions are different from neutral species can be seen dramatically by a comparison of H_3O^+ and its isoelectronic neutral NH_3. The calculated spontaneous infrared emission rate of NH_3 at an excitation of 3 eV is only 1.1(+2) s^{-1}, or a factor of 20 less than that of the isoelectronic ion. Although more information on infrared intensities would certainly be desirable, it seems safe to say that the earlier estimation of Herbst (1982*a*) that radiative stabilization rates of complexes would not greatly exceed 1.0(+2) s^{-1} is in error. A more reasonable estimate at this juncture would be to utilize the range of values shown in Figure 1 at any given vibrational energy. Thus, for a complex at an energy of 4 eV above the zero-point level, the range of stabilization rates (equated to radiative emission rates) would be 1(+3)–3(+3) s^{-1}. This increase will increase the calculated rate coefficients of all radiative association processes involving molecular ions except those already saturated at the collisional value or those that proceed via a different stabilization mechanism such as $C^+ + H_2$ (Herbst 1982*b*). It is interesting to note that the larger radiative stabilization rates were originally adopted by Herbst (1980*a*, *b*) before being discarded.

The spontaneous emission rates for molecular ions calculated above do not include overtone and combination transitions between vibrational levels and therefore may be below the actual rates. An extreme case of the importance of overtone transitions can be seen in H_3^+. The calculated spontaneous emission rate for this species is depicted in Figure 2 based on the theoretical intensities of Carney and Porter (1976). Neglect of the overtone transitions results in the usual linear spontaneous emission versus vibrational energy plot, whereas inclusion leads to a much stronger dependence on E_{vib} and significantly higher emission rates. It is expected that H_3^+ is an extreme case because of its small number of vibrational modes and resulting high energy per mode. In addition, there is evidence that the intensity of overtone transitions does not add to normal harmonic oscillator transitions but borrows intensity from them (Stine and Noid 1983), so that the actual spontaneous emission rate will be considerably closer to the value estimated by excluding overtone transitions. In any event, there is a finite possibility that the range of spontaneous emission rates advocated here based on our calculations of the two ions H_3O^+ and $HCNH^+$ may still be too low. To evaluate the contribution of overtone (and combination) transitions accurately, Herbst and Noid (1984) have begun a series of calculations of radiative stabilization rates by a totally different method from that utilized by Herbst (1982*a*). This new approach entails the use of fast Fourier transforms of dipole moment functions of classical trajectories representing molecular complexes.

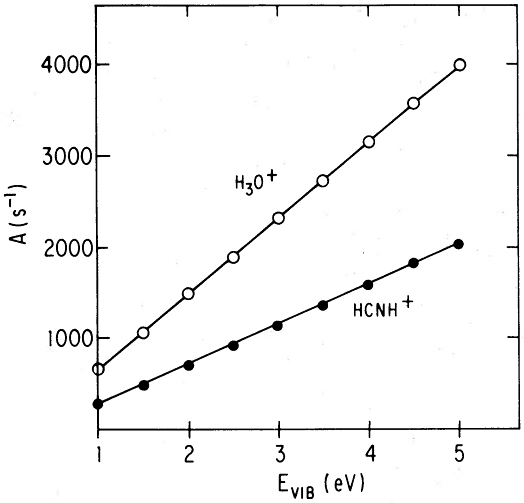

FIG. 1.—Spontaneous emission rates for molecular ions H_3O^+ and $HCNH^+$ plotted against vibrational energy.

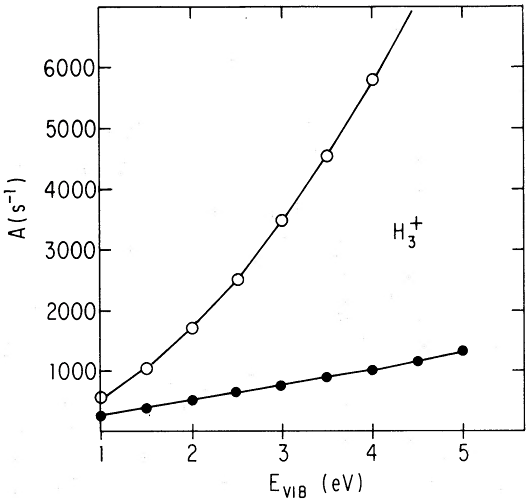

FIG. 2.—Spontaneous emission rate of ion H_3^+ plotted against vibrational energy, for the cases when overtones are ignored (*closed circles*) and included (*open circles*).

III. THE $CH_3^+ + H_2 \rightarrow CH_5^+$ ASSOCIATION

Barlow, Dunn, and Schauer (1984) have studied the radiative association of CH_3^+ and H_2 in the laboratory at 13 K and obtained a rate coefficient of 1.8(−13) $cm^3\ s^{-1}$. The most recent calculated value (Bates 1983*a*) for this rate coefficient is 3.3(−14) $cm^3\ s^{-1}$ at 10 K. The discrepancy does not appear to be particularly large given the uncertainties in the theoretical treatment. However, it must be noted that the experimental rate pertains to what is known as "normal" hydrogen, in which the ortho/para ratio remains at the high temperature value of 3:1. The calculated value pertains to hydrogen at strict thermal equilibrium in which the ortho/para ratio is determined by the temperature. At the temperature of the experiment, "normal" hydrogen consists of three parts $J = 1$ and one part $J = 0$, where J is the angular momentum quantum number, whereas equilibrium hydrogen is virtually all in the

TABLE 1

ADOPTED RADIATIVE ASSOCIATION RATE COEFFICIENTS

k_{RA} (10–50 K)

k_{RA} (cm^3 s^{-1}) = $a(T/300)^{-b}$

REACTANTS	COEFFICIENTS		REFERENCE
	a	b	
$C^+ + H_2$	4.0(−16)	0.2	1
$C^+ + C_3$	1.0(−13)	1.0	2, 3
$C^+ + C_4$	1.0(−09)	0.0	2, 3
$Na^+ + H_2$	4.0(−19)	0.0	4
$Na^+ + H_2O$	1.4(−17)	1.3	4
$NO^+ + H_2$	6.7(−20)	1.0	5
$HS^+ + H_2$	1.4(−16)	0.6	5
$OCS^+ + H_2$	6.1(−20)	1.5	5
$HCO^+ + H_2O$[a]	4.0(−13)	1.3	5
$HCO^+ + CH_4$	4.6(−14)	1.5	5
$CH_3{}^+ + H_2$	3.0(−14)	0.5	6, 7
$CH_3{}^+ + CO$	1.2(−13)	1.3	6
$CH_3{}^+ + H_2O$	5.5(−12)	1.7	6
$CH_3{}^+ + HCN$	9.0(−9)	0.5	6 (unmodified)
$CH_3{}^+ + NH_3$[a]	9.4(−10)	0.9	6
$CH_3{}^+ + CH_3OH$[a]	1.0(−08)	0.0	5 (unmodified)
$H_3O^+ + C_2H_4$	2.4(−13)	2.3	5
$CH_5{}^+ + CO$[a]	7.2(−14)	2.3	5
$C_2H_2{}^+ + H_2$	1.5(−14)	1.0	8
$C_2H_2{}^+ + CO$	1.1(−15)	2.0	9 (unmodified)
$H_2CN^+ + C_2H_2$	2.2(−15)	2.0	5
$C_3H^+ + H_2$	3.3(−13)	1.0	10
$C_3H^+ + CO$	1.1(−14)	2.0	9 (unmodified)
$C_2H_3{}^+ + CO$	2.0(−15)	2.5	9 (unmodified)
$H_3CO^+ + CH_4$	6.1(−16)	1.5	5
$C_3H_2N^+ + C_2H_2$	1.1(−9)	0.0	5
$C_2H_5{}^+ + H_2O$[a]	9.5(−13)	2.5	5

[a] These reactions have competing exothermic pathways which may, in some instances, dramatically reduce the radiative association rate coefficient (Bates 1983*b*; LHH). Further calculations on this point are planned.

REFERENCES.—(1) Herbst 1982*b*; (2) Bates 1983*b*; (3) Freed, Oka, and Suzuki 1982; (4) Smith *et al.* 1983; (5) LHH; (6) Bates 1983*a*; (7) Barlow, Dunn, and Schauer 1984; (8) Herbst 1983; (9) Herbst, Smith, and Adams 1984; (10) Herbst, Adams, and Smith 1984.

$J = 0$ state. The overall experimental rate coefficient at 13 K can be written as

$$k_{\text{expt}} = 0.75k(J = 1) + 0.25k(J = 0)\,, \qquad (2)$$

where the individual k's on the right-hand side of the equation refer to rate coefficients with molecular hydrogen in a particular J state. The theoretical rate coefficient is just $k(J = 0)$. According to the most detailed treatment of association reactions (Bass, Chesnavich, and Bowers 1979), the association-rate coefficient with hydrogen in its $J = 1$ state will be smaller than the rate coefficient with hydrogen in its $J = 0$ state. Thus the overall experimental rate coefficient should be smaller than the theoretical rate coefficient. If we assume the $J = 1$ rate to be so much smaller than the $J = 0$ rate that it can be ignored, then the experimental rate coefficient should be a factor of 4 smaller than the theoretical rate coefficient. Thus the discrepancy between current theory and experiment is worse than it actually appears. In addition, the theory when applied to the analogous three-body association-rate coefficient is actually too large by a factor of 3 at 300 K (Bates 1983*a*). It would thus appear that the discrepancy in the radiative association case is due to the estimated radiative stabilization rate.

In the calculation of Bates (1983*a*), the radiative stabilization rate of the $CH_5{}^+$ complex is set at 200 s^{-1}. According to current thermodynamic values (Herbst 1980*a*), the $CH_5{}^+$ complex is formed with an energy of approximately 2 eV. Based on the calculated spontaneous emission rates for the other ions discussed above, it would seem reasonable to up the radiative stabilization rate for $CH_5{}^+$ to ~1000 s^{-1}. This increase of five in the radiative stabilization rate changes the calculated equilibrium rate coefficient for $CH_5{}^+$ radiative association at 10 K to 1.6(−13) cm^3 s^{-1}. The equilibrium rate coefficient at this temperature inferred from the experimental measurement will be in the range 1.8(−13)–7.2(−13) cm^3 s^{-1} depending on the contribution of $k(J = 1)$. The resulting discrepancy between theory and experiment is smaller than previously thought and can probably be accounted for by a further increase in the radiative stabilization rate. Quantum chemical calculations of the infrared intensities of $CH_5{}^+$ are urgently needed. It should be noted that if the radiative association rate of $CH_3{}^+ + H_2$ approaches 7.2(−13) cm^3 s^{-1} at 10 K, the abundance of the $CH_3{}^+$ ion will be significantly diminished over current model estimates (e.g., Leung, Herbst, and Huebner 1984), which, in turn, may lead to diminished estimates for certain complex molecules with ion–molecule syntheses based on this ion.

IV. UPDATED RATE COEFFICIENTS

A significant number of calculated radiative association rates have appeared in the literature previously (Bates 1983*a*, *b*; LHH, and references therein). It is suggested that these rates be increased to reflect the higher radiative stabilization rates for ionic molecular complexes. In Table 1 we have included a list of updated radiative association rates, many of which have appeared in the literature with values at 10 K only. We have arbitrarily assumed that the radiative stabilization rate is 1.0(+3) s^{-1} for all reactions in which the complex is formed with an energy of ≈ 2 eV or more above the ground state and 5.0(+2) s^{-1} if this energy is in the range 1–1.5 eV. The estimated temperature dependence in the range 10–50 K has been included based on the analysis of Bates (1983*a*), which takes into account possible subthermal excitation in the internal energy modes of the reactants. For those reactions not studied by Bates (1983*a*) or whose temperature dependence has not previously been investigated in some detail, we have approximated his treatment as follows. The temperature dependence has been estimated by either the thermal treatment (Herbst 1980*a*) or the modified thermal treatment (Herbst 1980*b*), depending on whether the neutral species is polar or nonpolar respectively. Sub thermal excitation, if present, has been handled by evaluating the rotational partition functions of the reactants at their effective rotational temperatures rather than at the kinetic temperature of the cloud. Finally, the calculated rates in the range 10–50 K have been fitted to simple power laws for inclusion into model libraries. As an example consider the reaction between HCO^+ and H_2O. Since H_2O is strongly polar, the thermal theory is used to predict a temperature dependence of $T^{-x+0.5}$, where x refers to the rotational degrees of freedom of the reactants. However, the linear ion HCO^+ has a large dipole moment and is expected to be subthermal in its rotational energy level distribution with an effective rotational temperature that does not exceed 10 K, so that it contributes no additional temperature dependence. Water,

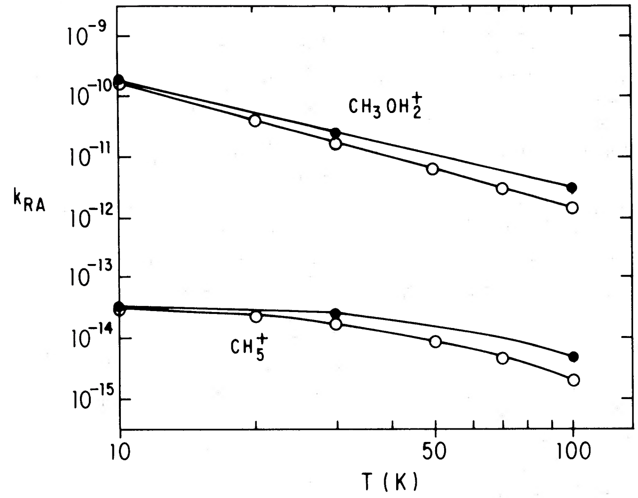

FIG. 3.—Temperature dependences of Bates 1983*a* (*closed circles*) and of this work (*open circles*) compared for radiative associations of ions CH_5^+ and $CH_3OH_2^+$.

another polar species, is expected to have most of its population in its ground state and its first excited metastable state. Its partition function has been calculated with that assumption, which leads to a value of x equal to 0.8 in the range 10–100 K. Therefore the total predicted temperature dependence for this reaction is $T^{-1.3}$. To gauge the accuracy of our approach to temperature dependence, we have compared our results with those of Bates (1983*a*) for two association reactions leading to the ions $CH_3OH_2^+$ and CH_5^+. The comparison is depicted in Figure 3, where our results are labelled by open circles and Bates's by closed circles. The two treatments are assumed to produce equal rate coefficients at 10 K. (The rate coefficients at 10 K shown in Fig. 3 do not contain the new radiative stabilization rates.) In general our temperature dependences appear to be slightly more severe but the agreement is quite good. Note that the association reaction leading to CH_5^+ does not possess a rate coefficient with a simple power law for its temperature dependence over the plotted range of 10–100 K. Even for such systems we have approximated the temperature dependence as a power law in the 10–50 K range. Users should be wary of extrapolating our tabulated results to temperatures much higher than 70 K.

It is to be hoped that quantum chemists will calculate fundamental intensities for more ionic species so that more accurate rate coefficients can be determined. Such calculations may lead to even larger rate coefficients than are tabulated here.

Note added in manuscript 1984 November 12.—Rogers and Hillman (1982, *J. Chem. Phys.* **77**, 3615) have recently calculated IR vibrational intensities for both HCO^+ and HOC^+. Use of our theory then leads to spontaneous emission rates at a vibrational energy of 4 eV of 1×10^3 s^{-1} for HCO^+ and 5×10^3 s^{-1} for HOC^+.

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