

PROSPECTS FOR THE INVOLVEMENT OF TRANSITION METALS IN THE CHEMISTRY OF DIFFUSE INTERSTELLAR CLOUDS: FORMATION OF FeH^+ BY RADIATIVE ASSOCIATION*

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(First received 26 February 1990; in final form 2 April 1990)

ABSTRACT

Transition metals traditionally have been ignored in chemical models of interstellar clouds. Thermochemical considerations indicate that the formation of several important species can be catalyzed by transition metal ions. The importance of such chemistry depends critically upon the rate of conversion of atomic metal ions into molecular species. Potential energy curves and transition moments have been calculated and a simple model employed to determine the rate constant for the appropriate reaction of iron, FeH^+ formation by radiative association.

INTRODUCTION

Physical processes in interstellar clouds are of general astronomical interest because of their implications for the formation of stars and planets from such clouds. Chemistry within these objects is interesting both in its own right and because of the interrelationship between chemical and physical conditions; chemical observations can lead to conclusions about cloud temperature, pressure and history. For example, chemical considerations have led to the consensus that most clouds suffer severe mechanical shocks, and constitute important evidence that solid, granular material is present in substantial amounts [1].

The reliability of such inferences naturally depends upon the completeness of the reaction networks used to model cloud chemistry. Except for simple charge exchange, reactions of metals are given little consideration in such networks [2,3]. This neglect is in general given no justification in the literature, but it probably originates in the metals' relatively low abundances and largely unknown chemistry under the exotic conditions required. Recently, however, advances have been made in understanding the chemistry of isolated, gas-phase metal ions [4]. In addition, the low metal abundances indicate only that

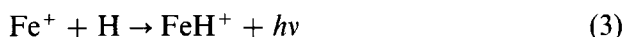
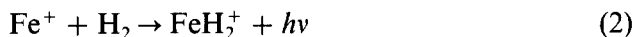
*Contribution No. 7933.

metal-containing species are rare, not that they are unimportant; rare elements may affect the chemistry of more abundant elements through catalytic cycles. We consider herein some possibilities for transition metal reactivity in diffuse clouds. The discussion centers on iron because it is the most abundant transition metal.

Primary reactions of iron

Diffuse clouds typically have temperatures of ≈ 100 K and number densities of 10^1 – 10^3 cm^{-3} [1]. Hydrogen comprises most of any diffuse cloud, and H atoms shield the bulk of the cloud from UV radiation at frequencies above the Lyman limit. Atoms with ionization potentials below 13.6 eV, however, are efficiently photoionized, and are present principally as ions. Discussion of metal chemistry therefore centers around ion chemistry. Only ground state ions need be considered, since the time between collisions is weeks to years, and excited states have ample time for radiative relaxation. Ternary processes can be ignored at these pressures. Although molecules that contain transition metals could conceivably originate on grains [5], it is unlikely that such reactive species would be released from cold grains in substantial quantities. (Recently, a careful search towards ζ Oph yielded no evidence for gas-phase NaH or MgH) [6].

Since hydrogen is by far the most abundant element in the interstellar medium [1], we first consider reactions of Fe^+ with H or H_2



Reaction 1 may be dismissed immediately, since it is endothermic by 56 kcal mol^{-1} [7,8]. The remaining two reactions are radiative associations of small molecules, which are generally slow. In addition, since the ground state of Fe^+ is 6D and the sextet states of FeH_2^+ are presumably repulsive, reaction 2 is spin-forbidden and will be exceedingly slow. Reaction 3 is probably the fastest of these processes, and we therefore consider FeH^+ formation to be the point of entry into Fe^+ chemistry.

Secondary reactions of iron

Several reactions of FeH^+ with the more abundant neutral atoms (H, O, C, and N) may be envisioned. Moreover, the products are important molecules in chemical models of diffuse clouds. Reaction 4 produces H_2 , considered the “primordial” molecule. If metal-catalyzed formation of H_2 is significant, there is less need to invoke surface chemistry on grains to explain H_2 formation.



Likewise, main-group gas-phase reactions produce a lower [NH]/[OH] ratio than do surface reactions, and this ratio is therefore used to gauge the importance of grain chemistry [9]. High NH abundances do not require grains if metal ion catalysis is important.

As mentioned above, diffuse clouds are shielded from higher-frequency UV light by atomic hydrogen. Species with high ionization potentials can nevertheless be ionized by cosmic rays. The cosmic ray ionization rate is usually inferred from the abundance of either OH or HD [10]. Estimates of this rate require revision if metals can generate OH or HD in significant amounts.

Reactions 4–7 are quite exothermic, and may be expected to proceed near the collision rate. Reaction 8, however, may be eliminated; laboratory experiments have demonstrated that it does not occur on the timescale of seconds at ≈ 300 K [11].

FeH⁺ formation by radiative association

The rate of reaction 3 is essential for evaluating the expected importance of Fe⁺ chemistry. For example, if radiative association were efficient, catalysis by Fe⁺ would produce too much OH to be consistent with observations.* As one would expect, however, radiative association reactions of atoms are generally slow, and experimental rate measurements are extraordinarily difficult. Most values have therefore been calculated rather than measured [12,13]. To calculate the rate of radiative association of Fe⁺ and H, we have used an approach based upon the method by Bates [14a], as developed by Solomon and Klemperer [14b]. We have calibrated this method by calculating the rate of radiative association of C⁺ and H. The best current value for this latter reaction is approximately $3.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ (The 0 K rate was estimated by extrapolation of data from ref. 15). We use this value as a benchmark for assessing the reliability of our calculation.

* If radiative association proceeded at the collision rate, significant contributions would be expected from reactions of iron: $1.6 \times 10^{-5} \text{ cm}^{-3}$ to [OH], $1.8 \times 10^{-6} \text{ cm}^{-3}$ to [NH], $1.7 \times 10^{-6} \text{ cm}^{-3}$ to [CH], and 0.042 cm^{-3} to [H₂]. The assumptions used to derive these values are described in the Results and Discussion.

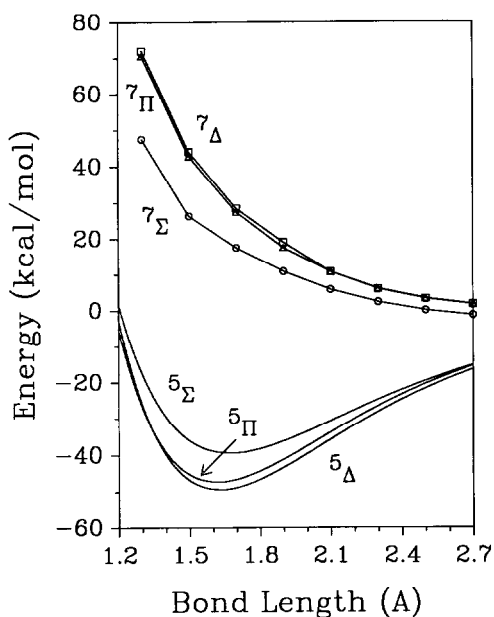


Fig. 1. Calculated potential energy curves for FeH^+ . For the quintet states, best-fit Morse potentials (constrained to the D_e values of ref. 18) are shown.

CALCULATIONAL DETAILS

The rate calculation follows the method of Solomon and Klemperer [14b] with some simplifications. Essentially the same procedure has recently been applied to calculate the radiative association rates for $\text{C}^+ + \text{O}$ and $\text{C} + \text{O}$ [16]. In this model, the ground state atoms enter along one of the possible diabatic molecular potential energy curves. The reaction is considered to have taken place when a transition occurs to a lower electronic state. For FeH^+ , the atomic states are $\text{Fe}^+(\text{}^6D)$ and $\text{H}(\text{}^2S)$, and the corresponding bound molecular states are $\text{}^5\Delta$, $\text{}^5\Pi$, and $\text{}^5\Sigma$. The septet states are all repulsive (see Fig. 1) and do not contribute to the reaction.

The transition probability is integrated over all classical trajectories with impact parameter b less than the classical critical value [17] $b_c = (2q^2 \alpha/E)^{1/4}$. The integrated probability $P(T)$ is multiplied by the Langevin collision rate [17] k_L to yield a value for the temperature-dependent rate constant. Equations 9 and 10 indicate the expressions for k_L and $P(T)$.

$$k_L = 2\pi q(\alpha/\mu)^{1/2} \quad (9)$$

$$P(T) \propto \int_0^\infty dv \int_0^{b_c} db \int_{r_0}^\infty dr |\mathbf{D}(r)|^2 [U_2(r) - U_1(r)]^3 \times \quad (10)$$

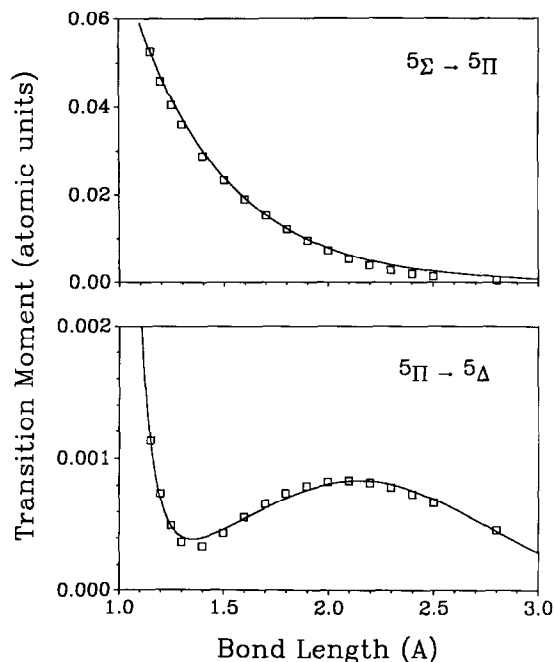


Fig. 2. Calculated electric dipole moment functions for transitions in FeH^+ . Top: Transition from $^5\Sigma$ to $^5\Pi$. Bottom: Transition from $^5\Pi$ to $^5\Delta$. Solid lines are fits of convenient expressions to the calculated values.

$$v^2 \exp(-\mu v^2/2kT) b/b_c^2 [v^2 - 2U_1(r)/\mu - v^2 b^2/r^2]^{-1/2}$$

In these equations, q is the elementary charge, α is the polarizability of the hydrogen atom, μ is the reduced mass of FeH^+ , and r_0 is the classical turning radius as determined from the effective potential. The potential energy functions $U_1(r)$ and $U_2(r)$ are Morse potentials generated by least-squares fits to results of ab initio calculations on the three lowest states of FeH^+ . The ab initio calculations were done at the DCCI-GEOM level as previously described by Schilling et al [18]. Electric dipole moment functions $\mathbf{D}(r)$ were calculated between states at the GVB(1/2) level, and spin-orbit coupling was ignored. The potential energy and dipole moment functions are displayed in Figs. 1 and 2. Fine structure and multiplicity factors are included, as discussed in ref. 14b. An additional factor of 2 accounts for the multiplicity of the final states. No attempt is made to account for tunneling through the centrifugal barrier. At 0 K, the integrals over v and b reduce to unity, simplifying the expression for the case $P(0)$.

For comparison with the accepted rate for the radiative association of C^+ and H, the 0 K rate for CH^+ formation was calculated using the model just

described. For this molecule, the Morse parameters for $U_1(r)$ and $U_2(r)$ were derived from least-squares fits to the experimental potential energy curves of Helm et al. [19], and the electric dipole moment function was a curve fit to ab initio results of Larsson and Siegbahn [20].

Techniques of much greater sophistication are necessary if accurate temperature dependence is desired [15,21]. The simple model that we have chosen can only be expected to yield an approximate rate constant. Fortunately, this is sufficient to allow us to assess the importance of metal ion chemistry in interstellar clouds. Accurate rates are only necessary for reactions that are found to be significant.

RESULTS AND DISCUSSION

Potential energy curves

For rate calculations, the Morse potentials were fit with D_e constrained to the values of ref. 18. This yields $D_e = 49.4, 47.3$ and $39.4 \text{ kcal mol}^{-1}$, $r_e = 1.63, 1.62$ and 1.67 \AA , and $a = 1.59, 1.59$ and 1.49 \AA^{-1} for the ${}^5\Delta$, ${}^5\Pi$, and ${}^5\Sigma$ states, respectively. If the fit is unconstrained, we obtain instead $D_e = 61.0, 57.3$ and $45.8 \text{ kcal mol}^{-1}$, $r_e = 1.65, 1.64$ and 1.68 \AA , and $a = 1.39, 1.41$ and 1.38 \AA^{-1} . These values for r_e and a are more reliable than those from the constrained fit since they describe the bonding region more accurately. The unconstrained fits lead to predictions of $\omega_e = 1690, 1650$ and 1450 cm^{-1} (the ordering expected from the literature D_e values [18]) and $\omega_e x_e = 33.5, 34.0$ and 32.8 cm^{-1} for the ${}^5\Delta$, ${}^5\Pi$, and ${}^5\Sigma$ states [22].

Comparison with previous calculations [23,24] suggests that our bond lengths are too large by $\approx 0.04 \text{ \AA}$, probably because less correlation is included at the DCCI-GEOM level. For the ${}^5\Delta$ state, our ω_e value of 1690 cm^{-1} is probably too low; Pettersson et al [23] find 1817 cm^{-1} and Sodupe et al. [24] find 1830 cm^{-1} . The latter study, however, found vibrational frequencies ranging from 1578 to 1928 cm^{-1} depending upon the level of calculation and the basis set, with no simple trends evident. It is difficult to assess the accuracy of our $\omega_e x_e$ values. We should also comment on the symmetry of the ground state of FeH^+ . A ${}^5\Delta$ ground state was found in two calculations [18,23] but ${}^5\Pi$ was found in the third [24]. We favor the conclusion of the earlier calculations because of the substantially better agreement of their calculated bond energies with experiment. In addition, our DCCI-GEOM calculations indicate a ${}^5\Delta$ ground state.

Radiative association rate

For the radiative association of C^+ and H , our calculated rate at 0 K is $2.3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$, 35% less than the reference value of $3.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$.

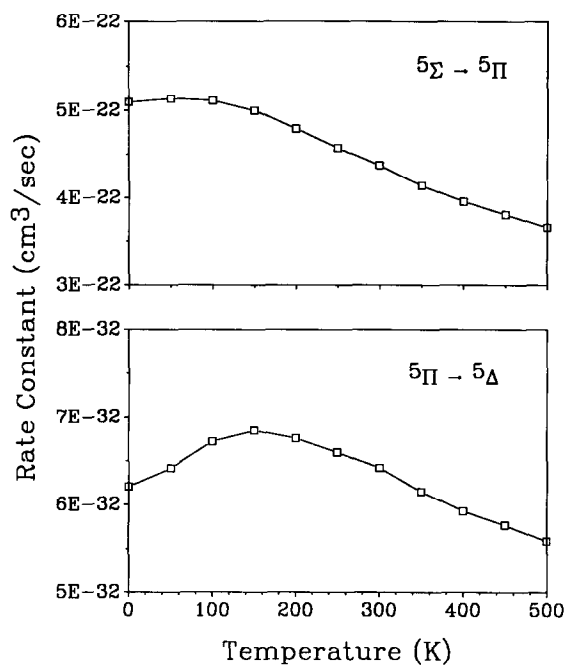


Fig. 3. Contributions to the rate of radiative association of Fe^+ and H. Top: Transitions from ${}^5\Sigma$ to ${}^5\Pi$. Bottom: Transitions from ${}^5\Pi$ to ${}^5\Delta$.

This agreement suggests that our values for FeH^+ will also be reliable. Our corresponding 0 K rate for FeH^+ is $5.1 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$. Tunneling [25] and vibrational relaxation are expected to increase this value only by small factors. Only a weak temperature dependence is predicted with this simple model, as illustrated in Fig.3. Essentially all reactive collisions involve a ${}^5\Sigma \rightarrow {}^5\Pi$ transition; the 0 K contribution for ${}^5\Pi \rightarrow {}^5\Delta$ transitions is only $6.2 \times 10^{-32} \text{ cm}^3 \text{ s}^{-1}$, 10 orders of magnitude less.

We can estimate the chemical consequences of this rate using typical abundances [1] and considering a cloud of total density 100 cm^{-3} . Reaction 4 is assumed to account for most of the FeH^+ destruction rate ($n_{\text{H}} = 54 \text{ cm}^{-3}$), although dissociative recombination and photodissociation will also contribute. If we assume further that reaction 4 proceeds at the collision rate k_{L} (with $n_{\text{Fe}} = 3.9 \times 10^{-5} \text{ cm}^{-3}$), then we expect a steady-state FeH^+ density of $9.0 \times 10^{-18} \text{ cm}^{-3}$. Assuming that photodissociation is the major loss mechanism for the neutral products, and estimating $k = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for reactions 5–7, this FeH^+ density leads one to expect iron chemistry to contribute $7.7 \times 10^{-18} \text{ cm}^{-3}$ to the OH density, $8.7 \times 10^{-19} \text{ cm}^{-3}$ to [NH], $8.3 \times 10^{-19} \text{ cm}^{-3}$ to [CH], and $1.9 \times 10^{-14} \text{ cm}^{-3}$ to $[\text{H}_2]$ (taking $A_{\nu} = 0.5 \text{ mag}$

and parameters for grain model 2 from ref. 26). It is clear from comparison with typical abundances ($n_{\text{OH}} = 5.2 \times 10^{-6} \text{ cm}^{-3}$, $n_{\text{CH}} = 3.5 \times 10^{-6} \text{ cm}^{-3}$, $n_{\text{H}_2} = 46 \text{ cm}^{-3}$) that these contributions are negligible, and that catalysis by radiatively associated FeH^+ is insignificant.

The reasons for the low radiative association rate can be gleaned from Eq. 10 and a chemical comparison of FeH^+ and CH^+ . The orbitals of transition metal hydride ions MH^+ are expected to be much more diffuse than those of CH^+ . As a result, overlap between states is less and the transition moment is reduced. In addition, the energy gap between electronic states [18] is expected to be much less for MH^+ than for CH^+ (for which the state splitting is 69 kcal mol^{-1}). Since the rate is proportional to the square of the transition moment and the cube of the state splitting, factors of 10^{-1} in these quantities lead to a factor of 10^{-5} in the rate. Comparison with CH^+ thus leads to an expected rate of roughly $10^{-22} \text{ cm}^3 \text{ s}^{-1}$, close to the calculated value. Radiative association reactions of transition metal ions with other atoms, such as oxygen, may have larger rate constants if the corresponding molecular state splittings are greater or if charge-transfer transitions are possible, but any increase in rate constant will probably be offset by the lower abundance of the neutral reaction partner.

Although we expect the radiative association of metal ions and neutral atoms to be very slow, small molecules such as O_2 and CO_2 may be better reaction partners. Millar has investigated the consequences of rate coefficients greater than $10^{-16} \text{ cm}^3 \text{ s}^{-1}$ for a number of associations involving main-group metal ions. If such reactions are efficient in dense clouds, then dissociative recombination with electrons will lead to enhanced neutral metal atom abundances and probably require downward revision of estimates of the fraction of metal depleted onto grains [27]. In diffuse clouds, neutral metal abundances may be increased by neutralization of the ions by large molecules such as polycyclic aromatic hydrocarbons (PAHs) [28].

We have considered only reactions involving the most abundant form of gaseous iron (Fe^+) with the most abundant neutral reaction partners (H and H_2). Since these reactions are found to be very slow, processes involving less-abundant species may be important. For example, reactions with oxygen to generate transition metal oxides such as TiO^+ , TiO [29] and FeO [30] have previously been considered, although interstellar searches for these molecules have been unsuccessful [30,31]. Another possibility is proton transfer to neutral Fe. Reaction 11 has been suggested by Merer et al. [30].



Since these proton transfer reactions are exothermic (molecular proton affinities were obtained from ref. 32), they are expected to occur rapidly.

CONCLUSIONS

Gas-phase transition metal chemistry is expected to mimic many of the reactions supposed to occur on grain surfaces. If transition metal ions can form molecules with moderate efficiency, then catalysis by metals will be important in diffuse interstellar clouds and substantial revision of chemical models will be required. However, we have calculated the rate constant for FeH^+ formation by radiative association to be only $5 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$. In general, radiative association rates of transition metal ions with atoms are probably negligibly slow. Unless faster routes into gas-phase transition metal chemistry are found, such chemistry may therefore be neglected in chemical models of diffuse interstellar clouds.

ACKNOWLEDGMENTS

We are indebted to J.-M. Langlois for indispensable assistance with the transition moment calculations, and to E.F. van Dishoeck and G.A. Blake for valuable comments and encouragement. We thank a referee for helpful comments, and the National Science Foundation for support under grants CHE-83-18041 (WAG) and CHE-87-11567 (JLB).

REFERENCES

- 1 W.W. Duley and D.A. Williams, *Interstellar Chemistry*, Academic, London, 1984. For metal abundances, see also: M.E. van Steenberg and J.M. Shull, *Astrophys. J.*, 330 (1988) 942.
- 2 (a) E.F. van Dishoeck and J.H. Black, in F.J. Millar and D.A. Williams (Eds), *Rate Coefficients in Astrochemistry*, Kluwer, Dordrecht, 1988, p. 209.
(b) W.D. Langer and T.E. Graedel, *Astrophys. J., Suppl. Ser.*, 69 (1989) 241.
- 3 B.E. Turner, *Astrophys. J.*, 314 (1987) 363.
- 4 (a) J.L. Beauchamp, in K.S. Suslick, (Ed), *High Energy Processes in Organometallic Chemistry*, ACS Symp. Ser. 333, American Chemical Society, Washington, DC, 1987, Chap. 2.
(b) P.B. Armentrout and J.L. Beauchamp, *Acc. Chem. Res.*, 22 (1989) 315.
- 5 A. Bar-Nun, M. Litman, M. Pasternak and M.L. Rappaport, in B.H. Andrew (Ed), *Int. Astron. Union Interstellar Molecules*, Symp. 87, Reidel, Dordrecht, 1980, p. 367.
- 6 J. Czarny, P. Felenbok and E. Roueff, *Astron. Astrophys.*, 188 (1987) 155.
- 7 J.L. Elkind and P.B. Armentrout, *J. Phys. Chem.*, 91 (1987) 2037.
- 8 D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd edn., Natl. Stand. Ref. Data Ser. 37, Natl. Bur. Stand., Washington, DC, 1971.
- 9 (a) A.P.C. Mann and D.A. Williams, *Mon. Not. R. Astron. Soc.*, 209 (1984) 33.
(b) R.M. Crutcher and W.D. Watson, *Astrophys. J.*, 209 (1976) 778.

- 10 (a) S. Lepp and A. Dalgarno, in *Astrochemistry*, Int. Astron. Union Symp. 120, Reidel, Dordrecht, 1987, p. 167.
- (b) E.F. van Dishoeck and J.H. Black, *Astrophys. J., Suppl. Ser.*, 62 (1986) 109.
- (c) A.P.C. Mann and D.A. Williams, *Mon. Not. R. Astron. Soc.*, 214 (1985) 279.
- (d) E.J. O'Donnell and W.D. Watson, *Astrophys. J.*, 191 (1974) 89.
- 11 T.J. Carlin, L. Sallans, C.J. Cassady, D.B. Jacobson and B.S. Freiser, *J. Am. Chem. Soc.*, 105 (1983) 6320.
- 12 D.R. Bates and E. Herbst, in F.J. Millar and D.A. Williams (Eds), *Rate Coefficients in Astrochemistry*, Kluwer, Dordrecht, 1988, p. 17.
- 13 E. Herbst, *Astrophys. J.*, 291 (1985) 226.
- 14 (a) D.R. Bates, *Mon. Not. R. Astron. Soc.*, 111 (1951) 303.
- (b) P.M. Solomon and W. Klemperer, *Astrophys. J.*, 178 (1972) 389.
- 15 M.M. Graff, J.T. Moseley and E. Roueff, *Astrophys. J.*, 269 (1983) 796.
- 16 A. Dalgarno, M.L. Du and J.H. You, *Astrophys. J.*, 349 (1990) 675.
- 17 T. Su and M.T. Bowers, in M.T. Bowers (Ed), *Gas Phase Ion Chemistry*, Vol 1, Academic, New York, 1979, Chapt. 3.
- 18 J.B. Schilling, W.A. Goddard III and J.L. Beauchamp, *J. Phys. Chem.*, 91 (1987) 5616.
- 19 H. Helm, P. Cosby, M.M. Graff and J.T. Moseley, *Phys. Rev. A*, 25 (1982) 304.
- 20 M. Larrson and P.E.M. Siegbahn, *Chem. Phys.*, 76 (1983) 175.
- 21 H. Abgrall, A. Giusti-Suzor and E. Roueff, *Astrophys. J. Lett.*, 207 (1976) L69.
- 22 G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 1, 2nd edn., Robert E. Krieger, Malabar, FL, 1989, pp. 100, 101.
- 23 L.G.M. Pettersson, C.W. Bauschlicher, Jr. and S.R. Langhoff, *J. Chem. Phys.*, 87 (1987) 481.
- 24 M. Sodupe, J.M. Lluch, A. Oliva, F. Illas and J. Rubio, *J. Chem. Phys.*, 90 (1989) 6436.
- 25 I.W.M. Smith, *Astrophys. J.*, 347 (1989) 282.
- 26 E.F. van Dishoeck, in F.J. Millar and D.A. Williams (Eds), *Rate Coefficients in Astrochemistry*, Kluwer, Dordrecht, 1988, p. 49.
- 27 T.J. Millar, in M.F. Kessler, J.P. Phillips and T.D. Guyenne (Eds), *Galactic and Extragalactic Infrared Spectroscopy*, Eur. Space Agency SP-192 (preprints), 1982, p.33.
- 28 A. Dalgarno, *Int. J. Mass Spec. Ion Processes*, 81 (1987) 1.
- 29 M. Oppenheimer and A. Dalgarno, *Astrophys. J.*, 212 (1977) 683.
- 30 A.J. Merer, C.M. Walmsley and E. Churchwell, *Astrophys. J.*, 256 (1982) 151.
- 31 T.J. Millar, J. Eildér, Å. Hjalmarsen and H. Olofsson, *Astron. Astrophys.*, 182 (1987) 143.
- 32 S.G. Lias, J. Liebman and R.D. Levin, *J. Phys. Chem. Ref. Data*, 13 (1984) 695.