

## ROTATIONAL EXCITATION OF MOLECULAR IONS IN INTERSTELLAR CLOUDS\*

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### ABSTRACT

Rate constants for rotational excitation of  $N_2H^+$  by low-energy collisions with He have been obtained from accurate quantum mechanical calculations. Rates for excitation of  $HCO^+$  and rates for excitation by collisions with  $H_2$  are expected to be qualitatively similar. The excitation rate for molecular ions is found to be only slightly faster than that for similar neutral species, and not much faster as had been previously suggested. The implications of this for interpreting microwave observations of interstellar  $N_2H^+$  and  $HCO^+$  are discussed.

*Subject headings:* atomic and molecular processes — molecules, interstellar

### I. INTRODUCTION

Radioastronomical observations of molecular rotational spectra are providing new insights into the nature of the interstellar gas. For example, it now appears that a significant fraction of galactic matter resides in cool "dense clouds" in which *molecules* are the dominant species. The dynamics of these clouds must therefore be understood in terms of what are traditionally considered *chemical* processes. Although the fractional ionization in these objects is generally low, it is now recognized (Herbst and Klemperer 1973; Watson 1973) that ion-molecule reactions play an important, and possibly a dominant role in interstellar chemistry. The reason for this is simple: ionic species have much longer range (electrostatic) interactions than do neutral molecules, and this leads to rate constants for ion-molecule reactions which are typically two to three orders of magnitude faster than neutral-neutral reactions.

Many molecular ions are expected to be as abundant in interstellar clouds as observed neutral species, and radio observations of these should provide valuable information. A difficulty, however, is the nearly complete lack of laboratory measurements of microwave rotational frequencies for ions. (For a recent exception see Dixon and Woods 1975). Nonetheless, based on theoretical molecular structure calculations, two molecular ions have tentatively been identified as the carriers of observed interstellar lines:  $HCO^+$  (Klemperer 1970; Wahlgren *et al.* 1973; Snyder 1975) and  $N_2H^+$  (Turner 1974; Green *et al.* 1974; Turner and Thaddeus 1975).

In order to interpret observed interstellar spectra in terms of local physical conditions such as number density and kinetic temperature, one must consider the process of spectral line formation, and this, in turn, requires a knowledge of rates for radiative and collisional excitation. (For optically thick lines it is also necessary to consider radiative trapping.) The

radiative rates are simply related to the molecular electric dipole moment; although dipole moments for ionic species cannot be measured with current techniques, they can be computed to the necessary accuracy from quantum theory (see, e.g., Green 1974). Collisional rates are difficult to measure for both neutral and ionic species, and the lack of accurate values is currently a major source of uncertainty in interpreting radioastronomical data. It has been assumed, however, that collision cross sections for rotational excitation will be much larger—20 to 30 times larger—for ionic than for neutral species (Herbst and Klemperer 1974; Turner 1974). The reasoning behind the assumption of greatly enhanced excitation rates for molecular ions can be summarized as follows: Rate constants for ion molecule reactions are typically  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , whereas the fastest neutral molecule reaction rates are about  $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Assuming reaction at every collision, these rates then represent the basic collision frequency for ionic and neutral species, respectively. Since rotational excitation is also expected to occur at essentially every collision, this leads immediately to the postulated factor of 25 enhancement for ionic over neutral excitation rates.

The rapid collision frequency for ionic species can be understood semiquantitatively in terms of a critical impact parameter for orbiting collisions due to the long-range charge-induced dipole interaction (Gioumoussis and Stevenson 1958). This maximum impact distance is simply computed in terms of collision parameters, and for  $N_2H^+$ -He at 30 K it is 6.4 Å, corresponding to a collision rate of  $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . For neutral collisions, the simplest approximation is a hard-sphere model with a critical impact distance equal to the van der Waals radius, i.e., about 3 Å for HCN-He. This model predicts neutral collision rates only about 5 times smaller than ionic rates. At low energies the long-range  $R^{-6}$  attractive force for neutral systems would reduce this difference even further. The neutral reaction rate of  $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  quoted above, on the other hand,

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corresponds to a maximum impact parameter of only 1.8 Å (assuming a reduced mass appropriate to HCN–He and a kinetic energy corresponding to 30 K), implying that such neutral reactions are not, in fact, occurring at every collision. A better experimental estimate for neutral collision rates can be found in measurements of collision-induced spectral pressure broadening. For CO–He and HCN–He, for example, these correspond to cross sections of about 30 Å<sup>2</sup> or excitation rates of about 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup> (cf. Green and Thaddeus 1974, 1975), and are thus in substantial agreement with the hard-sphere model outlined above.

It would seem, then, that the conventional argument that excitation of molecular ions is about 25 times faster than excitation of neutral species is incorrect. Rather, it would appear that excitation of ionic species is only a few times faster than that of neutral species. A similar conclusion was reached independently by Woods *et al.* (1974) based on considerations of semiclassical pressure broadening theory. These conjectures have found some experimental justification in the observations of Dixon and Woods (1975), who note that collisional pressure broadening of microwave spectra for ionic species is comparable to that found for neutral species. Finally, this conclusion has now been substantiated by accurate quantum mechanical calculations for rotational excitation of N<sub>2</sub>H<sup>+</sup> in low-energy collisions with He.

The theoretical calculation of collision cross sections requires (1) determination of the intermolecular potential between target and projectile, and (2) determination of collision dynamics on this potential. Both of these problems are amenable to available computational techniques for many of the systems of astrophysical interest (Green and Thaddeus 1975), and calculations have recently been presented for collisional excitation of HCN (Green and Thaddeus 1974), which is structurally similar to N<sub>2</sub>H<sup>+</sup>. The calculation of the N<sub>2</sub>H<sup>+</sup>–He interaction potential and collision dynamics is discussed in the next section. Results are presented in § III, where they are compared with the HCN results. Excitation rates for N<sub>2</sub>H<sup>+</sup> are found to be about 3 to 4 times faster than those for HCN, as suggested above, except at the very lowest temperatures, where the N<sub>2</sub>H<sup>+</sup> rates exceed those for HCN by *at most* a factor of 10. On the other hand, the “propensity rules” or relative probabilities for different quantum transitions are markedly different for the two systems. Astrophysical implications of these findings are discussed in § IV.

## II. DETAILS OF CALCULATION

The relevant computational techniques for intermolecular potentials and collision dynamics have been discussed at some length by Green and Thaddeus (1975), and will be reviewed only briefly here. The interaction potential is obtained by computing the electronic energy of the N<sub>2</sub>H–He<sup>+</sup> complex as a function of nuclear positions. For low-energy rotational excitation the rigid rotor approximation is adequate, and it suffices to vary only the position of

He relative to N<sub>2</sub>H<sup>+</sup> fixed at its equilibrium geometry. The electronic potential energy surface for N<sub>2</sub>H<sup>+</sup>–He has been computed within the molecular orbital (Hartree-Fock) approximation. This method is known to reproduce accurately the short-range repulsive (exchange) forces. It also accurately reproduces the long-range induction (moment-induced moment) forces, but not the dispersion forces. For neutral systems, the latter dominate the long-range potential so that molecular orbital methods cannot be used; for ionic systems, however, the induction forces are expected to dominate at all distances, and molecular orbital methods should be adequate for the entire surface (cf. Lester 1970).

For reasons of economy, a relatively small basis set (self-consistent field) expansion was used to approximate the Hartree-Fock wave functions. In particular, N<sub>2</sub>H<sup>+</sup> was described by a “double-zeta” basis (which includes two functions for each occupied *n*l shell in the separated atoms), and He was described by double-zeta plus “polarization” (*p* functions which allow the He charge distribution to be polarized by the permanent electric moments of the N<sub>2</sub>H<sup>+</sup>).<sup>1</sup> Such calculations are expected to give a semiquantitative description of the interaction. In particular, the short- and long-range anisotropies which determine rotational excitation are expected to be within 20–40 percent of their true values. This is consistent with the level of accuracy expected in the scattering calculations which will be described below.

The interaction potential was computed for a number of distances *R* and angles  $\Theta$  (measured from the center of mass of N<sub>2</sub>H<sup>+</sup>, with  $\Theta = 0$  corresponding to linear NNH–He); these are given in Table 1. For the scattering calculation the angular dependence was fitted to the usual Legendre polynomial expansion by minimizing the root-mean-square *average* deviation; six terms in the expansion gave a good fit for all distances. Continuous radial functions were obtained by fifth-order polynomial interpolation plus an exponential extrapolation at short distances and an inverse power extrapolation at large distances. The long-range terms obtained this way are in good agreement with the leading terms of the usual long-range perturbation theory expansion:

$$\begin{aligned} V_0^{\text{LR}}(R) &= -q^2\alpha/2R^4 - \dots \\ V_1^{\text{LR}}(R) &= -2q\mu\alpha/R^5 - \dots \\ V_2^{\text{LR}}(R) &= -(3qQ + \mu^2)\alpha/R^6 - \dots, \end{aligned}$$

where *q*,  $\mu$ , and *Q* are the charge, dipole, and quadrupole, respectively, of the molecular ion, and  $\alpha$  is the polarizability of He. In this context it should be noted that a self-consistent field calculation will always give

<sup>1</sup> The contracted double-zeta Gaussian bases of Dunning (1970) plus He 2*p*(1.0) and He 2*p*(0.2) were used for all geometries. Calculations were done with the MOLECULE-SCF programs written by J. Almlöf (University of Uppsala, Sweden) and P. S. Bagus (IBM Research Laboratory, San Jose, California), and required approximately one minute per geometry on an IBM 360/95. We are grateful to U. Wahlgren and P. S. Bagus for providing a copy of these programs.

TABLE 1  
 $N_2H^+-He$  INTERACTION POTENTIAL  $V(R, \Theta)$   $cm^{-1}$

$R/a_0$	$0^\circ$	$30^\circ$	$60^\circ$	$90^\circ$	$120^\circ$	$150^\circ$	$180^\circ$
3.5	+87800.00	+34050.00	+9413.000	+6229.000	+9092.000	+25760.000	+49730.000
4.0	+41000.00	+13010.00	+3309.000	+2101.000	+3312.000	+10070.000	+18640.000
4.5	+9643.00	+4314.00	+959.000	+602.200	+1067.000	+3505.000	+6554.000
5.0	+2042.00	+1131.00	+148.100	+100.900	+271.200	+1070.000	+2088.000
5.5	+76.15	+99.19	-88.000	-44.330	+16.680	+237.000	+536.100
6.0	-369.10	-173.10	-126.000	-71.980	-49.160	-12.730	+51.130
6.5	-396.10	-211.30	-107.800	-64.740	-55.300	-62.100	-60.130
7.0	-334.90	-185.90	-81.860	-51.350	-46.520	-55.520	-62.760
7.5	-260.70	-145.50	-61.010	-39.720	-36.210	-40.820	-45.650
8.0	-187.80	-106.20	-45.860	-30.940	-27.650	-28.970	-31.160
8.5	-127.10	-74.83	-35.110	-24.360	-21.290	-21.070	-21.730
9.0	-83.61	-52.45	-27.430	-19.530	-16.900	-16.020	-16.020
9.5	-55.30	-37.31	-21.730	-15.800	-13.390	-12.510	-12.070
10.0	-37.74	-27.65	-17.340	-12.950	-10.970	-10.100	-9.660
10.5	-27.26	-21.18	-14.220	-10.750	-9.129	-8.273	-7.944
11.0	-20.52	-16.70	-11.720	-8.976	-7.659	-6.913	-6.627
11.5	-16.02	-13.45	-9.766	-7.571	-6.452	-5.859	-5.618
12.0	-12.84	-11.02	-8.185	-6.408	-5.486	-4.982	-4.784

the long-range induction interaction, to all orders of perturbation theory, but for the multipole moments and polarizabilities which would be calculated for the separated fragments with the same expansion basis set.

The short-range interaction for  $N_2H^+-He$  is quite similar to that found for  $HCN-He$ .<sup>2</sup> Both are dominated by even terms in the Legendre expansion (symmetric with respect to  $\Theta = 90^\circ$ ); it should be recalled that, for  $HCN$ , this led to a strong propensity for  $\Delta J = 2$  transitions. The potential well occurs at about the same distance for both systems, but it is about 3 times deeper for  $N_2H^+$ . The long-range potentials, of course, differ considerably. As noted already, the isotropic interaction for the ionic system is of relatively long range, falling off as  $R^{-4}$ , while that for the neutral system decreases as  $R^{-6}$ . The long-range anisotropy of the ionic system is dominated by the  $P_1$  term which is much stronger and of much longer range than its counterpart in the neutral system. The long-range  $P_2$

<sup>2</sup> Because the  $HCN-He$  interaction was obtained from a uniform electron gas model (Gordon and Kim 1972; Green and Gordon 1974), it is interesting to compare the predictions of this model with the more rigorous self-consistent field interaction for  $N_2H^+-He$ ; this is done in the Appendix.

anisotropies are rather similar for the two systems, but for the neutral system this is the dominant term.

Collision dynamics were treated within the quantum close-coupling framework (Arthurs and Dalgarno 1960). The major approximation is then truncation of the target rotational basis set used to expand the total wave function. However, computed cross sections must converge as one includes more (energetically higher) target levels in the calculation (Miller 1971). In previous studies, adequate convergence has been obtained by including all energetically accessible levels (open channels) plus the lowest one or two inaccessible levels (closed channels). Unfortunately, convergence here appears to be less satisfactory, as can be seen in Table 2, where cross sections at representative energies are given as a function of basis set size. (An expansion basis which includes target rotational levels  $j = 0$  through  $j = n$  is denoted  $Bn$ .)

The reason for the poorer basis set convergence here compared with earlier calculations would appear to be due to the increased depth of the potential well relative to the rotational energy spacings of the target, which increases the importance of Feshbach resonances (see, e.g., Burke *et al.* 1969). The scattering calculation is done for a specified *total* energy at which a certain

TABLE 2  
 CROSS SECTIONS ( $\text{\AA}^2$ ) AS A FUNCTION OF BASIS SIZE\*

Energy $cm^{-1}$	$j \rightarrow j'$	$B4$	$B5$	$B6$	$B7$	$B8$
6.0	$0 \rightarrow 1$	134.0	116.0	112.0	104.0	122.0
18.0	$0 \rightarrow 1$	80.4	61.9	50.9	71.6	39.8
	$0 \rightarrow 2$	46.3	48.7	53.4	47.4	58.5
	$1 \rightarrow 2$	80.6	71.6	69.5	67.4	61.1
30.0	$0 \rightarrow 1$	...	...	45.0	42.5	37.9
	$0 \rightarrow 2$	...	...	51.0	45.2	43.1
	$0 \rightarrow 3$	...	...	26.2	24.0	29.5
	$1 \rightarrow 2$	...	...	51.1	56.2	54.0
	$1 \rightarrow 3$	...	...	31.2	29.4	32.2
	$2 \rightarrow 3$	...	...	49.4	40.1	37.6

\*  $Bn$  indicates a basis which includes target rotational levels  $j = 0$  through  $j = n$ .

number of target rotational levels are (asymptotically) energetically accessible, with the remaining energy being allocated (asymptotically) to relative kinetic energy. During the collision, however, additional energy from the interaction potential can be converted into internal rotational energy of the target, so that there will (temporarily) not be enough kinetic energy available to separate target and projectile; this leads to relatively long-lived collision complexes (Feshbach resonances). One might expect such complexes to produce an essentially statistical distribution of final target states, in contradistinction to the HCN calculations, where one found distinct "propensity rules" related to the relative size of various terms in the Legendre expansion of the interaction potential. In more classical language, for "hard" collisions of short duration, such as appeared to be the case for HCN-He, one expects an impulsive torque to be applied to the target which reflects the shape of the interaction; whereas for collisions of long duration one expects a statistical redistribution of the available energy into all degrees of freedom. Indeed, the  $N_2H^+$ -He calculations show evidence of such a statistical probability of final states.

For the final calculations, at least three closed levels were included for collision energies below  $65\text{ cm}^{-1}$ ; cross sections at higher energies were estimated with a *B7* basis. Although the basis set convergence is poorer than might be desired, this source of error is estimated to introduce uncertainties of less than 50 percent in the final rate constants. Such accuracy is adequate to answer the immediate astrophysical questions which require a knowledge of the overall rate of excitation by collisions and a qualitative idea of the relative probabilities of different transitions.

### III. RATE CONSTANTS

Using the interaction potential and scattering calculations described in the previous section, cross sections for rotational excitation have been computed for a range of collision energies. These have been averaged over Boltzmann distributions to obtain rate constants which are presented in Table 3. From a consideration of the sources of error discussed in the previous section, these rates are believed to be within 50 percent of the correct values.

It is interesting to compare the rates for  $N_2H^+$ -He collisions with those found for the structurally similar HCN-He system (Green and Thaddeus 1974). Two points are particularly noteworthy: First, rates for excitation of the ionic species are only *slightly* larger than those for the neutral system. For example, if one considers the most probable transitions out of the lowest rotational level— $R(0 \rightarrow 1)$  for  $N_2H^+$  and  $R(0 \rightarrow 2)$  for HCN—then, except at the lowest temperatures ( $\leq 10\text{ K}$ ) where transition energy effects become important, excitation of the ion is only 2 to 3 times faster than excitation of the neutral molecule. This conclusion is not changed if one considers instead the *total* rate of excitation out of the lowest level; the enhancement of the ionic over neutral excita-

tion is then about a factor of 4. This is consistent with the simple models presented in the Introduction, but it is contrary to the previous assumption of a factor of 20–30 enhancement for ions. The second comparison concerns the probability for different quantum transitions; whereas the overall excitation rates are comparable for both systems, the propensity rules differ markedly. For  $N_2H^+$  all energetically allowed transitions have similar probabilities. While single quantum jumps are generally most likely, the probability for multiple quantum transitions falls off slowly with increasing  $\Delta J$ . This is in sharp contrast with HCN, where a strong propensity for  $\Delta J = 2$  transitions was found.

As noted previously, the essentially statistical probability for different quantum transitions in  $N_2H^+$  is attributed to the formation of relatively long-lived collision complexes for the ionic, but not for the neutral system. An alternate explanation for this phenomenon has also been considered: the short-range interactions for both systems are similar, being dominated by even terms in the Legendre expansion which are expected to favor even  $\Delta J$  transitions. The ionic system, however, also has an important long-range  $P_1$  term which is absent in the neutral system. It seemed possible that the even  $\Delta J$  transitions in  $N_2H^+$  were due to short-range interactions, just as in HCN, whereas the odd  $\Delta J$  transitions were due to the long-range interaction. To examine this possibility, the  $N_2H^+$ -He scattering calculations were repeated with a modified interaction potential in which the  $P_1$  term was forced rapidly to zero at distances beyond the potential minimum. This gave only small changes in the predicted propensity rules; cross sections for  $\Delta J = 1$  and  $\Delta J = 2$  transitions were still found to be similar for low-energy collisions.

### IV. DISCUSSION

Rate constants have been computed for rotational excitation of  $N_2H^+$  by collisions with He at the low temperatures of interstellar clouds. These rates are important for interpreting radioastronomical observations of molecular ions. Of course, the extraction of detailed information such as isotopic abundances and local temperatures and densities from these observations is complicated by considerations of radiative trapping and cloud geometries. Therefore, only a few qualitative points will be considered here.

The most significant finding of this study is that the overall rate for excitation of  $N_2H^+$  is only slightly larger than that for similar neutral species, and not much larger as had previously been conjectured. In this context it should be noted that  $HCO^+$ —presumably the carrier of the X-ogen line—is structurally very similar to  $N_2H^+$ , and both of these ions are expected to have essentially the same excitation cross sections. Thus one must discount the conjecture of Herbst and Klemperer (1974) that the failure to detect isotopically substituted  $H^{13}CO^+$  may be related to an enhanced collisional excitation rate which "tightly couples" the brightness temperature of the ions to the kinetic temperature. Also, Turner's (1974) initial estimate of

TABLE 3  
 RATE COEFFICIENTS  $R(j \rightarrow j')$ \*

$j$	$j'$						
	0	1	2	3	4	5	6
$T = 5 \text{ K}$							
0.....	...	1.2790	0.1740	0.0087	0.0002	0.0000	0.0000
1.....	1.0435	...	0.5160	0.0201	0.0003	0.0000	0.0000
2.....	0.5100	1.8527	...	0.1328	0.0036	0.0000	0.0000
3.....	0.2667	0.7542	1.3901	...	0.0562	0.0003	0.0000
4.....	0.1651	0.3527	1.0561	1.5623	...	0.0133	0.0001
5.....	0.0677	0.2946	0.4800	0.6362	0.8101	...	0.0058
6.....	0.0998	0.3363	0.6348	0.6454	0.8656	1.0544	...
$T = 10 \text{ K}$							
0.....	...	1.8074	0.6719	0.1410	0.0195	0.0013	0.0001
1.....	0.9454	...	1.2035	0.2031	0.0242	0.0028	0.0002
2.....	0.5144	1.7626	...	0.5676	0.0886	0.0067	0.0006
3.....	0.2946	0.8148	1.5509	...	0.3641	0.0238	0.0017
4.....	0.1906	0.4513	1.1175	1.6876	...	0.1484	0.0102
5.....	0.0996	0.3961	0.6564	0.8509	1.1382	...	0.0943
6.....	0.1059	0.3583	0.6889	0.7431	0.9713	1.1690	...
$T = 20 \text{ K}$							
0.....	...	2.0639	1.1900	0.5189	0.1908	0.0446	0.0113
1.....	0.8660	...	1.7359	0.5892	0.2023	0.0680	0.0164
2.....	0.4657	1.6240	...	1.1108	0.3918	0.1061	0.0297
3.....	0.2835	0.7721	1.5515	...	0.8765	0.1865	0.0472
4.....	0.1989	0.5044	1.0348	1.6612	...	0.5099	0.1146
5.....	0.1162	0.4258	0.7070	0.8886	1.2776	...	0.3548
6.....	0.0958	0.3320	0.6400	0.7287	0.9294	1.1494	...
$T = 30 \text{ K}$							
0.....	...	2.1390	1.3424	0.7617	0.3981	0.1415	0.0505
1.....	0.8329	...	1.8954	0.8042	0.4069	0.1912	0.0688
2.....	0.4200	1.5282	...	1.3769	0.6125	0.2569	0.1064
3.....	0.2662	0.7258	1.5378	...	1.1545	0.3537	0.1398
4.....	0.1968	0.5184	0.9617	1.6251	...	0.7632	0.2492
5.....	0.1203	0.4209	0.6988	0.8610	1.3159	...	0.5590
6.....	0.0888	0.3126	0.5976	0.7026	0.8872	1.1577	...
$T = 40 \text{ K}$							
0.....	...	2.1906	1.3710	0.9026	0.5657	0.2515	0.1058
1.....	0.8211	...	1.9524	0.9211	0.5742	0.3172	0.1392
2.....	0.3835	1.4620	...	1.5330	0.7505	0.3963	0.1977
3.....	0.2525	0.6898	1.5308	...	1.3227	0.4807	0.2389
4.....	0.1924	0.5227	0.9082	1.6041	...	0.9442	0.3653
5.....	0.1219	0.4130	0.6869	0.8347	1.3478	...	0.7180
6.....	0.0842	0.2976	0.5639	0.6806	0.8568	1.1872	...

\* In units of  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .

local hydrogen density from an analysis of observed  $\text{N}_2\text{H}^+$  brightness temperatures must be revised. Assuming the same kinetic temperature as Turner,  $T_k = 30 \text{ K}$ , and no radiative trapping,  $\text{H}_2$  densities of  $10^5 \text{ cm}^{-3}$  are required to produce the observed brightness. Furthermore, using Turner's parameters for "dark dust clouds" with the revised rates gives an excitation temperature only 0.1 K above the background for the 0–1 transition, so that failure to detect  $\text{N}_2\text{H}^+$  in these objects is not surprising.

Collisional propensity rules are generally different

from selection rules for radiative transitions, and competition between these two processes can lead to a variety of non-Boltzmann (non-LTE) distributions among molecular energy levels. A number of interstellar spectra display apparent non-LTE behavior, and collisional pumping mechanisms have been suggested to explain some of these. For example, the HCN 0–1 transition is split into three hyperfine components which can be resolved in some astrophysical sources; and anomalous intensity ratios have been observed. Kwan and Scoville (1975) have shown that the observed

intensities can be explained by collisional pumping together with a simple model of radiative trapping. Their argument depends explicitly on the  $\Delta J = 2$  collisional propensity rule found for HCN; it does not work if  $\Delta J = 1$  transitions are as probable as double quantum jumps. Therefore, this mechanism is not applicable to  $N_2H^+$ , which shows the same hyperfine structure as HCN (if the small additional structure due to the inner nitrogen can be ignored).

The discussion so far has been based on excitation of  $N_2H^+$  by collisions with He. In interstellar clouds the most important projectiles are  $H_2$  molecules, which are 4 times more abundant than He atoms. It has been argued that excitation by low-energy collisions with  $H_2$  will be qualitatively similar to excitation by He, although perhaps faster by as much as a factor of 2 (see, e.g., Green and Thaddeus 1974). This argument is certainly valid for para- $H_2$ , since the lowest  $J = 0$  level is spherically symmetric, and excitation to higher levels is not energetically possible; the interaction potential and collision dynamics must then be qualitatively similar to He. On the other hand, ortho- $H_2$  is metastable, and the  $J = 1$  level supports a long-range  $H_2$  quadrupole interaction. The leading long-range  $N_2H^+-H_2$  ( $J = 1$ ) interaction is then the charge-quadrupole, but this, like the charge-induced dipole, exerts no torque on the ion. The next term, however, is the dipole-quadrupole interaction, and this does exert torque on the ion. To a first approximation this term

has "dipole selection rules" for excitation of the ion, so that it is expected to enhance the probability of  $\Delta J = 1$  transitions. It is believed that the differences between  $H_2$  and He projectiles will not invalidate the qualitative conclusions presented here, but detailed calculations have been initiated to examine this conjecture more rigorously.

Finally, the importance of excitation by low-energy collisions with electrons should be considered. Cross sections for this process can be obtained within the Coulomb-Born approximation, as discussed by Chu and Dalgarno (1974), who give explicit formulas for evaluating these quantities. Here  $\Delta J = 1$  transitions are induced by interaction of the electrons with the dipole moment of the ion; and  $\Delta J = 2$  by interaction with the quadrupole moment. Unlike excitation by collisions with neutrals, excitation by electrons is qualitatively different for ionic and neutral molecules. For the former, the cross sections at threshold are non-zero, and in general quite large. Although the rate constants for excitation by electrons are about three orders of magnitude larger than those for excitation by neutrals, the fractional abundance of electrons is too low (Herbst and Klemperer 1974) for this to be a significant process in dense molecular clouds.

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## APPENDIX

Because it is generally necessary to determine the interaction at a large number of points on the potential energy hypersurface, rigorous *ab initio* calculations can become quite expensive. In previous work (on HCN, Green and Thaddeus 1974; and on CO, Green and Thaddeus 1975), extensive use has been made of a simple model based on a uniform electron gas, proposed by Gordon and Kim (1972). Although quite simple and much cheaper than molecular orbital approximations, this model appears to be satisfactory for closed-shell systems and for distances inside the potential minimum. It does not, however, correctly account for induction or dispersion forces, and, in previous calculations, perturbation theory has been used for the long-range forces and the electron gas model for the short-range forces.

The choice of self-consistent field calculations for  $N_2H^+$  was based on two considerations: First, because of the importance of induction forces for ionic systems, it was felt that the Gordon-Kim method might be inadequate over much of the potential surface, whereas the self-consistent field approximation is particularly suited to these forces. Secondly, the electron gas calculation using the computer program of Green and Gordon (1974) is somewhat more expensive for ionic than for neutral systems, since a slightly finer numerical integration grid then appears to be necessary.

In order to increase the data base for judging the accuracy of the electron gas model, it seemed desirable to compare the predictions of this model with the self-consistent field results for  $N_2H^+-He$ , at least in those regions where the short-range repulsive forces dominate. Accordingly, the short-range interaction was recomputed using the Gordon-Kim method. For electron charge distributions of the separated systems, a double-zeta, Slater orbital  $N_2H^+$  function was used along with an accurate Hartree-Fock function for He. In Figure 1 the self-consistent field results are compared with the electron gas "Hartree-Fock" energy both without and with the self-exchange correction advocated by Rae (1973). The Gordon-Kim method also includes a correlation term to correct the Hartree-Fock energy; as expected, this term was found to be a small fraction, less than about 25 percent, of the interaction energy, and reasonably constant in this region.

In comparing the results in Figure 1, it should be borne in mind that neither the self-consistent field nor the electron gas calculations here are at their theoretical limit due to the small expansion basis sets used, and that this may introduce uncertainties which are comparable to the differences between methods. Nonetheless, these results taken together with a growing body of similar comparisons (Green *et al.* 1975, and references therein) seem to imply, at least at the Hartree-Fock level, that the electron gas model is

