

TABLE I. Rotational constants in cm^{-1} for the HCN dimer ν_1 band. The quoted errors in the last digit(s) represent one standard deviation σ .

B_v	$(B'' - B')/10^{-5}$	$D_v/10^{-8}$	
$\nu = 0$ 0.058 215(2)		7.14(18)	Ref. 8
0.058 233 93		7.013(52)	Ref. 20
0.058 233 1(75)		6.8(2.4)	this work
$\nu = 1$ 0.058 176(2)	3.93(3)	7.14(17)	Ref. 8
$\nu = 2$ 0.058 165 1(75)	6.80(27)	9.3(2.4)	this work
ts			

formation about the structure of the complex, an investigation of the linewidth provides insight into the dynamics of the dissociation process. Since the observed dimer signals are negative, an upper limit for the lifetime of the excited metastable state is given by their flight time of roughly 90 μs from the molecular beam-laser crossing point to the bolometer. If internal vibrational redistribution is excluded, the linewidth can be interpreted as an inverse lifetime. A first analysis shows that when the multipass arrangement is used, the linewidth is clearly instrument limited, placing a lower limit of roughly 11 ns on the lifetime. Presently, attempts are being made to use a single laser crossing, therewith increasing the instrumental resolution by a factor of 3. Also, intensive searches are under way for the ν_2 band in the overtone. This band will be particularly interesting since it exhibits substantial broadening already in the fundamental.

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Effect of indistinguishable nuclei on product rotational distributions: The $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$ reaction^{a)}

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Although conservation of electron spin (multiplicity^{1,2}) and of orbital symmetry (the Woodward-Hoffmann rules³) are celebrated examples where symmetry considerations restrict the possible outcomes of a chemical reaction, almost no experimental examples are known where the presence of indistinguishable nuclei limits the form of the product distribution.^{4,5} We report what appears to be the first such instance. We have studied the hydrogen atom bimolecular exchange reaction $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$ and we observe a marked alternation in the populations of the even (para) and odd (ortho) rotational levels of the H_2 product.

Bimolecular exchange reactions are normally treated by

considering each particle to be distinguishable. However, this treatment must be modified when the collision complex contains identical nuclei.⁴⁻⁶ For example, let us consider the process $\text{A} + \text{AB} \rightarrow [\text{A}_2\text{B}] \rightarrow \text{A}_2 + \text{B}$. If the identical nuclei A are fermions, i.e., have half-integral nuclear spin ($I = 1/2, 3/2, \dots$), then the interchange of A results in a change of the sign of the total wave function ψ_{tot} . If the identical nuclei A are bosons, i.e., have integral spin ($I = 0, 1, \dots$), then the interchange of A causes ψ_{tot} to be unchanged. The transient $[\text{A}_2\text{B}]$ complex may be considered to be a nonrigid molecule subject to the symmetry classifications of the complete nuclear permutation-inversion (CNPI) group.⁷ These sym-

metry considerations place constraints as to which final product states can be formed in any reaction having indistinguishable nuclei.

The symmetry restrictions based on permutation of nuclei are sharpened if the nuclear spin part of ψ_{tot} is so weakly coupled to the other degrees of freedom that it may be factored out of ψ_{tot} , i.e., $\psi_{\text{tot}} = \psi_{\text{nuc}} \psi_{\text{other}}$, thereby making the nuclear spin a constant of the motion. This approximation, which is almost always valid, is equivalent to assuming that no ortho-para conversion occurs during the reactive collision. Then, the behavior of ψ_{tot} under interchange of A may be found by considering separately the behavior of ψ_{nuc} and ψ_{other} .

To illustrate this, consider the case where $[A_2B]$ is a bent collision complex having equal A-B bond lengths. Let us suppose that the electronic and vibrational parts of the wave function are unchanged by interchange of A. If B is much heavier than A, then $[A_2B]$ is a near prolate top whose rotational wave function may be approximated as $|JK_aM\rangle$ where the total angular momentum J makes the projection K_a on the a axis (least-moment-of-inertia axis) of the top, and the projection M on the space-fixed quantization axis. The interchange of A is equivalent to the symmetry operation of a 180° rotation about the a axis, C_2^a . It is well known⁸ that $C_2^a |JK_aM\rangle = (-1)^{K_a} |JK_aM\rangle$. Thus, if only $K_a = 0$ (or even K_a) rotational levels of $[A_2B]$ were to decompose into A_2 and B, this requires that ψ_{nuc} must be antisymmetric (para) if A is a fermion and that ψ_{nuc} must be symmetric (ortho) if A is a boson. In other words, the A_2 reaction product would be found exclusively in the para (ortho) rotational levels if A is a fermion (boson). An example of this behavior is the photofragmentation of H_2CO into H_2 and CO .^{5,9}

In general, the rotational wave function for the $[A_2B]$ asymmetric top may be written as a linear combination of $|JK_aM\rangle$ basis functions, with the sum restricted to either even or odd K_a . In the case of a direct reaction, equal weights of even and odd K_a contribute to the formation of $A_2 + B$ from the breakup of $[A_2B]$. Then, the A_2 product is found

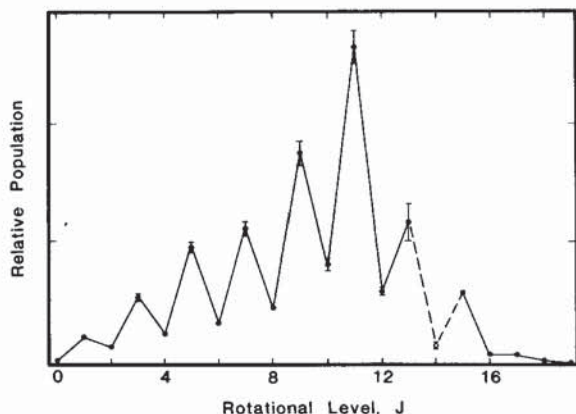


FIG. 1. Rotational distribution of the H_2 ($v=1$) product from the chemical reaction $H + HI$. The integrated, power-corrected ion signal is plotted against the rotational quantum number J . Error bars represent one standard deviation; where not visible, the error bar is the size of the point. The $J=14$ population (open circle) cannot be accurately determined in $(2+1)$ REMPI (Ref. 15).

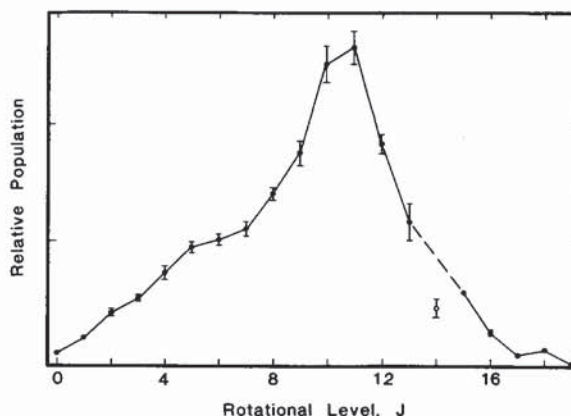


FIG. 2. Plot of the population in H_2 ($v=1, J$) versus J , corrected for the indistinguishability of the H nuclei in the $H + HI$ reaction. The populations of odd J levels have been divided by 3 to account for the ortho:para ratio of 3:1. Error bars represent one standard deviation.

with both symmetric and antisymmetric nuclear spin states in the ratio of their nuclear spin statistics, namely, $(I+1):I$. For the title reaction, $I=1/2$ (nuclear spin of H), and the ortho:para population ratio of the H_2 product is expected to be 3:1.

The present apparatus is the same as that used for our studies of the $H + D_2$ reaction.¹⁰⁻¹² Photolysis of HI at 266 nm generates translationally hot H atoms with center-of-mass collision energies of 1.6 and 0.68 eV in a concentration ratio of 2:1, corresponding to the concurrent production of $I(^2P_{3/2})$ and $I(^2P_{1/2})$, respectively. The H_2 product is detected by $(2+1)$ resonance enhanced multiphoton ionization (REMPI).^{13,14}

Figure 1 shows the rotational population distribution of the H_2 ($v=1$) product from $H + HI$. The population alternation between adjacent rotational levels is striking. Similar population alternations are found in the rotational distributions of the H_2 ($v=0$) and H_2 ($v=2$) products.

When the data of Fig. 1 are corrected for the indistinguishability of the H nuclei by dividing the odd J level populations by 3, the rotational distribution becomes smooth (Fig. 2). This result emphasizes that the observed rotational population alternation is a consequence only of nuclear spin symmetry in this reaction system, i.e., there are no dynamical symmetry constraints (resonances) in the intermediate complex.

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NOTES

Theoretical study of the far-infrared $A^3\Sigma_g^- \rightarrow X^3\Pi_u$ transition in Al_2

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Electronic structure calculations on Al_2 have predicted both a $^3\Pi_u$ ground state¹⁻³ and a $^3\Sigma_g^-$ ground state.^{4,5} However, in the most extensive theoretical calculations,² the prediction of a $X^3\Pi_u$ ground state was considered to be definitive despite the fact that the first excited state, $A^3\Sigma_g^-$, was computed to lie less than 200 cm^{-1} higher. This conclusion is consistent with the limited experimental information available. It is known from magnetic deflection experiments⁶ that the ground state of Al_2 is a triplet state. In matrix isolation absorption spectroscopy^{7,8} the well known $^3\Sigma_u^- \rightarrow ^3\Sigma_g^-$ emission band system⁹ is not observed. Cai *et al.*¹⁰ have observed two different electronic transitions of Al_2 in the fluorescence excitation spectrum of the products of laser vaporization of aluminum. The results are analyzed in terms of a $^3\Pi_u$ ground state: the observed vibrational frequency for the lower state of 284 cm^{-1} is lower than the experimental value (350.0 cm^{-1}) for the $^3\Sigma_g^-$ state, but in good agreement with the computed values¹⁻³ for the $^3\Pi_u$ state. Fu *et al.*¹¹ have studied the spectra of small aluminum clusters in a jet-cooled beam using the technique of resonant two-photon ionization with mass spectroscopic detection. Again, the well-known emission band system was not observed in absorption. Recently, Morse¹² has observed absorption in a jet-cooled beam from a lower state with $\Delta G_{1/2}$ of $300 \pm 2\text{ cm}^{-1}$. Since this vibrational frequency does not correspond well to that of either low-lying triplet state, it is possible that Morse is observing transitions within the singlet manifold. It is disconcerting, however, that different lower states are apparently observed in two different jet-cooled aluminum beams. Even though the body of experimental data supports the theoretical prediction¹⁻³ of a $X^3\Pi_u$ ground state for Al_2 , it would be desirable to establish this by direct spectroscopic observation as well as to determine the energy separation between the nearly degenerate $^3\Pi_u$ and $^3\Sigma_g^-$ states.

Since the $^3\Pi_u$ and $^3\Sigma_g^-$ states have opposite parity, there is no common excited state that is dipole connected to both

lower states. Thus unless a magnetic dipole or electric quadrupole transition can be observed, it will not be possible to position the states by observing a transition to a common upper state. However, in spite of the small separation and considerable difference in r_e of the two states, it might be possible to position the states by directly observing the $A^3\Sigma_g^- \leftrightarrow X^3\Pi_u$ transition in the far infrared. In this note, we report theoretical Einstein coefficients for this transition to aid experimentalists attempting to observe this transition.

The Gaussian basis used is the $(20s\ 13p\ 6d\ 4f)/(6s\ 5p\ 3d\ 2f)$ set from Ref. 2. The potential curves are obtained using complete-active-space self-consistent-field (CASSCF) multireference configuration-interaction (MRCI) wave functions. The active space for the CASSCF calculations consists of those molecular orbitals and six valence electrons derived from the atomic $3s$ and $3p$ orbitals. The MRCI calculations include all the configurations in the CASSCF as references. The transition moment is computed analogously, except that the CASSCF orbitals are determined using a state-averaged procedure with equal weights for the $^3\Pi_u$ and $^3\Sigma_g^-$ states, as a common molecular orbital basis set simplifies the calculation of the transition moment.

TABLE I. The transition moment function, in a.u.

$r\ (a_0)$	$\left\langle ^3\Pi_u \left \frac{(x+iy)}{\sqrt{2}} \right ^3\Sigma_g^- \right\rangle$
4.40	0.396 36
4.80	0.355 28
5.00	0.330 98
5.20	0.305 00
5.40	0.277 88
5.80	0.222 38
6.50	0.132 21