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State-resolved inelastic cross sections from CN $A\ ^2\Pi\ v=8$ to $X\ ^2\Sigma^+\ v=12$: Quenching of the even-odd alternation in the final rotational state populations

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An optical-optical double resonance technique has been employed for the study of collisional transfer from the CN $A\ ^2\Pi\ v=8$ manifold to $X\ ^2\Sigma^+\ v=12$ with initial and final rotational state resolution. In contrast to our previous studies of $v_A=3$ to $v_X=7$ and $v_A=7$ to $v_X=11$ collisions, no significant even-odd oscillation in the final X state rotational populations was observed for any of the incident A state levels investigated. The absence of this alternation for $v_A=8$ collisions is ascribed to the dependence on CN vibrational coordinate of the off-diagonal matrix element connecting the Σ and $\Pi(A')$ wave functions describing the CN(A,X)-Ar interaction. For all incident $v_A=8$ levels studied, a preference for formation of X state e vs f levels of a given N was observed.

I. INTRODUCTION

Optical-optical double resonance (OODR) experiments have provided considerable insight into the dynamics of collision-induced electronic transitions between the A and X states of CN^{1,2} and N₂^{3,4}. We have determined relative CN-Ar inelastic cross sections with initial and final CN rotational state resolution for transitions between the nearly isoenergetic $A\ ^2\Pi\ v=7$ and $X\ ^2\Sigma^+\ v=11$ manifolds,¹ as well as between $v_A=3$ and $v_X=7$,² which are separated by ~ 3 kT. Katayama has studied collisional transitions from $A\ ^2\Pi_u\ v=4$ to $X\ ^2\Sigma_g^+\ v=7^3$ and 8^4 in N₂⁺.

Alexander and Corey⁵ have recently outlined the general quantum treatment for collisional transitions between $^2\Pi$ and $^2\Sigma^+$ electronic states. They show that, in the absence of non-Born-Oppenheimer interactions in the isolated molecule, collisional interelectronic transfer is enabled by the off-diagonal electrostatic matrix element V_1 , which couples the two A' wave functions correlating with the Σ and Π state asymptotes. This matrix element depends on the relative separation and orientation of the scattering partners. Early theoretical treatments^{6,7} of $\Pi \rightarrow \Sigma$ collisional transitions considered only the lowest-order term in a multipolar expansion of V_1 . This induced-dipole term behaves like a Π - Σ transition dipole, and the strength of this coupling depends on the state mixing induced by non-Born-Oppenheimer interactions, such as are known to occur in CN.⁸ If this term were the dominant contribution to V_1 , then Π - Σ coupling would be significant only between spectroscopically perturbed levels.

The $A \sim X$ perturbation in CN causes a significant admixture of X state character in selected $v_A=7$ rotational levels because of crossings of $v_A=7$ and $v_X=11$ fine structure manifolds. In our experiments on $v_A=7$,¹ we find the collisional interelectronic $A \rightarrow X$ transfer rate to be comparable to that for purely rotational $A \rightarrow A$ transitions for all incident levels, independent of the degree of isolated-molecule

mixing. This result, along with Katayama's observation^{3,4} of facile $A \rightarrow X$ transfer in N₂⁺, where isolated-molecule mixing is symmetry forbidden, indicates the dominance of terms in V_1 beyond just the long-range induced-dipole term in allowing collisional interelectronic transfer to occur, at least for CN and N₂⁺. Similarly, this mechanism accounts for the rapid collision-induced electronic transitions observed⁹⁻¹¹ between triplet states of N₂.

The final X state rotational distributions in both CN^{1,2} and N₂^{3,4} clearly follow propensity rules which can be understood by the theoretical development of Alexander and Corey,⁵ for example, the absence of collisional transitions between s and a nuclear interchange symmetry levels in the homonuclear N₂⁺ molecule. We have observed an even-odd alternation in the CN final X state rotational populations. This alternation, which arises from the near homonuclear character of the CN-Ar interaction potentials, is particularly prominent in $v_A=3 \rightarrow v_X=7$ collisions.² A similar alternation was observed both experimentally¹² and theoretically¹³ in the final state populations in NO($X\ ^2\Pi$)-Ar pure rotationally inelastic collisions. Again, this oscillation is a result of the near homonuclear nature of the NO-Ar interaction potentials.¹⁴

By contrast, an even-odd alternation was observed for only a few incident CN rotational levels in $v_A=7 \rightarrow v_X=11$ collisions.¹ Because of the large energy gap between the $v_A=3$ and $v_X=7$ manifolds, the $v_A=3$ rotational levels for $N \lesssim 15$ possess very little X state character from the $A \sim X$ perturbation, while this mixing is larger in $v_A=7$, particularly for levels near a crossing between $v_A=7$ and $v_X=11$ fine-structure manifolds.⁸

In this paper, we extend our study of CN interelectronic collisions to $v_A=8 \rightarrow v_X=12$ transitions. Figure 1 displays the rotational energies in these two manifolds. Unlike the $v_A=7 \sim v_X=11$ isolated-molecule perturbation, the $^2\Pi\ v_A=8$ spin-orbit e/f parity manifolds cross the $^2\Sigma^+\ v_X=12\ e/f$ manifolds at "negative," rather than positive, values of J ; thus the mixing of these manifolds does not reach a maximum in a narrow range of J (which must of course be positive) about the crossing. Nevertheless, the degree of

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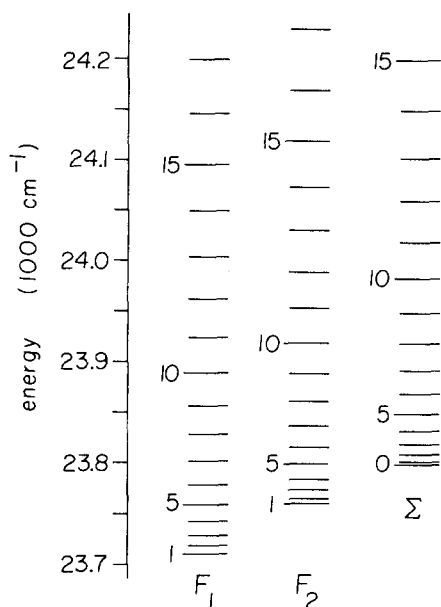


FIG. 1. Rotational energies (referred to the bottom of the $X^2\Sigma^+$ potential energy curve) of the $A^2\Pi v=8$ and $X^2\Sigma^+ v=12$ manifolds. Individual levels in the F_1 and F_2 spin-orbit manifolds of the A state and in the X state are denoted by the quantum number N , where $N = J - S$. The A state Λ doubling and X state spin splitting are not shown.

state mixing is significant over a wide range of rotational levels in the F_2e and F_2f fine-structure manifolds, with a maximum of 5.4% X state character (square of the probability amplitude) in the $N = 10 F_2e$ level.⁸ Our particular interest in carrying out these experiments is in determining the magnitude of the even-odd alternation in the final X state rotational populations as a function of initial level. We, in fact, find no significant alternation in the collisionally populated $v_X = 12$ manifold. While the $A \sim X$ isolated-molecule perturbation, can, in principle, quench these oscillations since it would mix, in the homonuclear molecule limit, levels of s and a nuclear exchange symmetry, the isolated-molecule mixing in both $v_A = 8$ and 7 is insufficient to explain the observed quenching. In the Discussion section, we offer an alternative explanation for the differences in the X state rotational distributions for $v_A = 8$ and 7, as compared to $v_A = 3$, incident levels.

II. EXPERIMENTAL

A detailed description of the experimental apparatus and OODR technique employed for the determination of state-resolved inelastic cross sections has been given previously.^{1,15} Cyanide free radicals are formed in approximately 2.2 Torr of argon by the addition of $\sim 1\%$ cyanogen to a flow containing metastable argon atoms, which are produced in a low-current dc discharge (200 V, 1 mA). The collision partner inducing inelastic collisions in CN is thus predominantly argon.¹⁵

Individual rotational levels in the $A^2\Pi v=8$ manifold were produced by pulsed irradiation on isolated lines in the $A-X$ (8,3) band¹⁶ near 599 nm by a Nd:YAG pumped dye laser. Collisionally populated levels in $v_A = 8$ and $v_X = 12$ were monitored by laser fluorescence detection employing the $B-A$ (9,8) and $B-X$ (9,12) bands near 492 nm with a XeCl excimer laser pumped dye laser. The pump and probe laser beams were overlapped spatially with a dichroic mirror; typical pulse energies were 40 and 2 mJ, respectively. The delay between the opening of the Nd:YAG Q switch and the firing of the excimer laser thyatron was controlled electronically, and the temporal delay between the ~ 10 ns long laser pulses, as observed with a photodiode and oscilloscope, was typically 10 to 20 ns. The OODR $B-X$ fluorescence signals were detected through a near UV filter (390 nm center wavelength, 10 nm bandpass) by an EMI 9813QB photomultiplier, whose output was converted to a dc signal by a boxcar averager.

In order to assign the lines in the OODR spectra, their absolute wave numbers were determined. Wave number differences were derived from simultaneous scans of the OODR spectrum and transmission maxima of a fused-silica Fabry-Perot étalon. The étalon free spectral range ($1.191 \pm 0.001 \text{ cm}^{-1}$) and absolute wave number markers were obtained using standard Ne lines in an optogalvanic spectrum of a hollow cathode lamp.

III. RESULTS

Figures 2 and 3 present probe laser scanned OODR fluorescence spectra when the two Λ doublets of $v_A = 8$, $N = 5$ F_1 are initially prepared in turn. The signal-to-noise ratio is

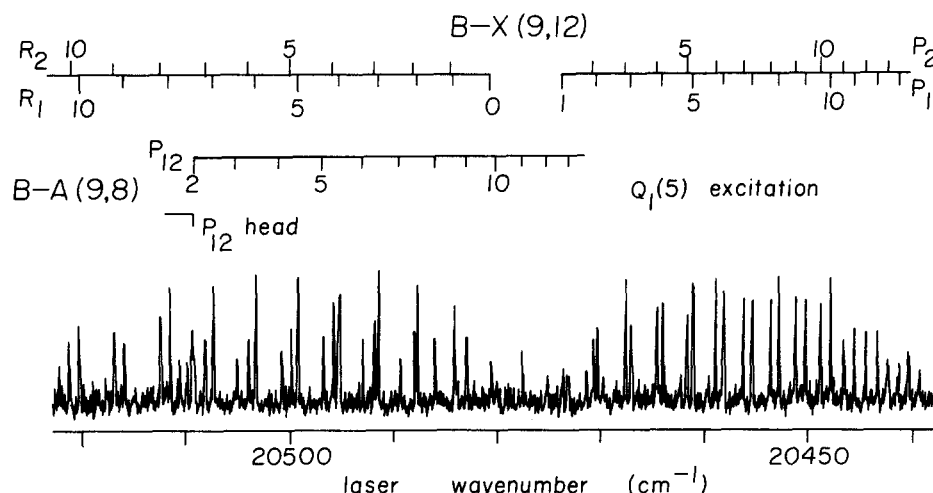


FIG. 2. OODR probe laser fluorescence excitation spectrum of the CN $B^2\Sigma^+-X^2\Sigma^+$ (9,12) and $B^2\Sigma^+-A^2\Pi$ (9,8) bands with the pump laser tuned to the $Q_1(5)$ line of the $A^2\Pi-X^2\Sigma^+$ (8,3) band. Individual lines are identified by the lower state quantum number N . The portion of the $B-A$ band to the blue is not shown. The pump-probe delay was 20 ns.

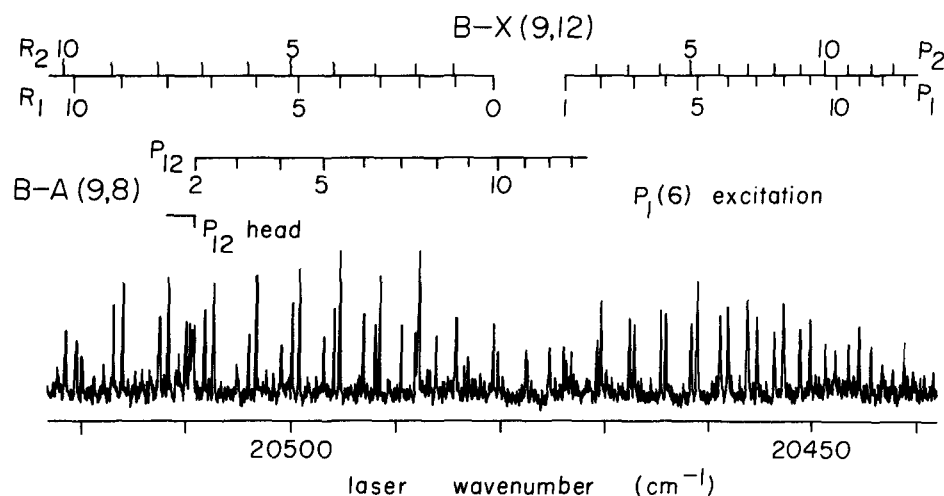


FIG. 3. OODR spectrum of the CN $B-A$ (9,8) and $B-X$ (9,12) bands with the pump laser tuned to the $P_1(6)$ line of the $A^2\Pi-X^2\Sigma^+$ (8,3) band. The pump-probe delay was 10 ns.

somewhat poorer in these spectra than in our previous studies,^{1,2} in part because an $A-X$ hot band with $v_X = 3$ is used for incident state preparation. Because the term energies of the $v_A = 8$ and $v_X = 12$ manifolds are very similar (see Fig. 1), the $B^2\Sigma^+-A^2\Pi$ (9,8) and $B^2\Sigma^+-X^2\Sigma^+$ (9,12) bands, which have been employed for determination of final rotational populations, are overlapped. In contrast to similar overlapping for $v_A = 7/v_X = 11$,¹ the $B-X$ band now lies to the red of the $B-A$ band. Despite the fact that the $B-X$ electronic transition moment is much larger than for the $B-A$ transition,¹⁷⁻²⁰ these bands have comparable strengths because of a large difference in Franck-Condon factors [0.076 and 0.012 for the $B-A$ (9,8) and $B-X$ (9,12) bands, respectively]. Since the spectrum of CN continues to be of interest and these bands have not been previously reported, we present in the Appendix our measured transition wave numbers of the observed rotational lines.

The $B-X$ rotational lines are prominent in the spectra in Figs. 2 and 3 and are indicative of significant $A \rightarrow X$ collisional interelectronic transfer from $v_A = 8$ to $v_X = v_A + 4$. In our previous study² of $v_A = 3$ collisions, we unsuccessfully searched for evidence of inelastic collisions to the lower $v_A - 1$ and $v_X = v_A + 3$ manifolds. In the present case, the $B-A$ (8,7) and $B-X$ (8,11) bands fall in the same spectral region as the bands under study. However, we did not see any rotational lines in these bands. These features would be visible in our OODR spectra despite the fact that these bands overlap with the $B-A$ (9,8) and $B-X$ (9,12) bands. We conclude that vibrational relaxation processes from $v_A = 8$ to $v_A = 7$ or $v_X = 11$ are at least an order of magnitude slower than the rate of collision-induced electronic transfer between the nearly isoenergetic $v_A = 8$ and $v_X = 12$ manifolds. This is consistent with the relatively small previously reported^{22,23} A state vibrational relaxation rates in comparison with $A \rightarrow A$ pure rotational and $A \rightarrow X$ interelectronic transfer rates.^{1,2}

We will concentrate here on the $B-X$ (9,12) band in order to study electronically inelastic collisions. However, we note from the comparable $B-X$ and $B-A$ fluorescence intensities and the similar magnitudes of the band strengths that the rate of collisional interelectronic transfer is compar-

able to that for pure rotational transfer, as was previously observed^{1,2} for other vibrational levels. The observed fluorescence intensities of individual rotational lines were converted to populations, as described in detail previously.¹ Because of the $A \sim X$ perturbation, lower-state eigenfunctions have both A and X state character; their probability amplitudes can be calculated from the $v_X = 12/v_A = 8$ Hamiltonian obtained by the analysis of Kotlar *et al.*⁸ The relative phase of the $B-X$ and $B-A$ transition moments, which is also required here for the calculation of fluorescence line strength factors, was obtained by measuring the relative intensities of strongly perturbed lines in the $B-A$ (8,7) and $B-X$ (8,11) bands, as well as through an *ab initio* calculation. The details of this experimental and theoretical determination of the relative phase and magnitudes of these electronic transition moments will be described in detail in a forthcoming publication.²¹

Because of the low signal-to-noise ratio in the present OODR spectra as compared to our $v_A = 3$ and 7 studies,^{1,2} we investigated fewer initial A state rotational levels which could be cleanly prepared by excitation of strong lines in the $A-X$ (8,3) band. Figure 4 displays the final rotational populations in the $v_X = 12$ manifold for several initially prepared $v_A = 8$ rotational levels. These populations represent sums over the e and f levels for each N value. These results were derived from an average over three to five separate OODR spectra. These distributions have a similar shape and width as those previously observed^{1,2} for $v_A = 3 \rightarrow v_X = 7$ and $v_A = 7 \rightarrow v_X = 11$ collisions. A range of final rotational levels is populated, but the average change of the rotational angular momentum is relatively small. Other initial levels with varying initial N were also investigated with poorer signal-to-noise ratio, and the derived populations (not shown) exhibited a correlation in the average final rotational energy with incident N , as was observed in the previous studies.^{1,2}

The most significant difference from the other incident v_A manifolds is the lack of observation here of an even-odd alternation in the final rotational populations vs N' , as was seen for $v_A = 7$,¹ and especially $v_A = 3$,² collisions. The slight fluctuations in the populations observable in Fig. 3 are within the estimated experimental uncertainties; in addition

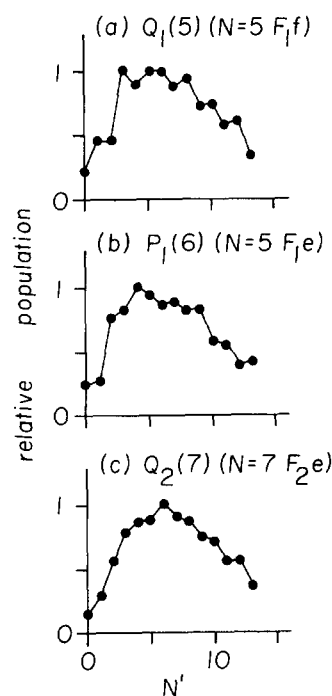


FIG. 4. Final state populations, summed over e and f levels, in the $v_x = 12$ manifold. The $A \sim X$ lines employed for excitation as well as the incident levels thus prepared, are identified. Each distribution is separately normalized to unity for the most probable level.

their phase is not constant over a given distribution. We note that the even-odd oscillation is missing both for relatively unperturbed initial levels, $N = 5 F_1 e$ and $F_1 f$ (calculated⁸ X state character 0.024% and 0.014%, respectively), as well as for a significantly perturbed level, $N = 7 F_2 e$ (X state character 5.03%).

Because of the large spin splitting in the $B \sim X$ (9,12) band arising from the $A \sim X$ perturbation (see the Appendix), the populations of the X state e and f levels of a given N can be separately determined. For all incident A state levels studied, a slight but definite preference, of the order of 30%, for formation of final e vs f levels is observed. Within our experimental uncertainties, a dependence on initial and final state quantum numbers could not be definitely established.

IV. DISCUSSION

With the results presented in this paper, we have now investigated collision-induced $A \rightarrow X$ electronic transitions in the CN molecule from three vibrational levels $v_A = 3, 7$ and 8 to $v_X = v_A + 4$. In all cases, this process is facile, with rates comparable to pure rotationally inelastic rates. The final X state rotational distributions are quite similar in general shape for comparable incident rotational levels in all three v_A manifolds, despite wide variation in the v_A/v_X energy gap. This suggests that it is the anisotropy of the CN-Ar interaction potentials, rather than energy resonant effects, that governs the change in rotational angular momentum.

The most significant difference between the present results and those^{1,2} for $v_A = 3$ and 7 is the absence here of the even-odd alternation in the final X state rotational populations for all incident A state levels excited. As discussed in detail previously,^{1,2} this oscillation is due to the near homonuclear character of the CN-Ar interaction potentials. In the homonuclear limit, transitions between levels of opposite

nuclear permutation symmetry are rigorously forbidden.⁵ In $D_{\infty h}$ symmetry, rotational levels in the X state of even and odd values of N would have s and a nuclear permutation symmetry, respectively, if this state were $^2\Sigma_g^+$, as in the isoelectronic N_2^+ molecule. Thus, transitions from incident A state levels which would have s and a symmetry in the homonuclear limit would be expected to populate collisionally even and odd N levels preferentially, respectively, in the X state, as has been observed in $v_A = 3$ and 7 collisions.^{1,2}

One possible explanation for the absence of the even-odd alternation in the final populations observed here for $v_A = 8$ collisions is the well-known $A \sim X$ perturbation in the isolated CN molecule.⁸ This perturbation mixes two electronic states which have opposite nuclear permutation symmetry in the homonuclear limit. (Hence this mixing between the $A \ ^2\Pi_u$ and $X \ ^2\Sigma_g^+$ states is forbidden in the isoelectronic N_2^+ ion.²⁴) The effect of this non-Born-Oppenheimer perturbation in CN is that the mixed levels will have an admixture of homonuclear s and a character. Collisions of such levels will hence exhibit a diminished even-odd alternation of final populations in collision-induced $A \sim X$ transitions. Unfortunately, while this mechanism is attractive in principle, the actual degree of electronic state mixing in the isolated CN molecule is not nearly sufficient to explain the complete absence of this oscillation, when compared especially to $v_A = 3$ collisions,² for which this state mixing is extremely small (of the order of 0.01%) because of the large $v_A = 3/v_X = 7$ energy gap. The degree of X state character in the incident A state levels studied in detail here is 0.014%, 0.024%, and 5.03% for $N = 5 F_1 f$, $N = 5 F_1 e$, and $N = 7 F_2 e$, respectively. It can be seen in Fig. 4 that no experimentally significant even-odd oscillation is present both for the relatively unperturbed incident F_1 levels and the comparatively strongly mixed $N = 7 F_2 e$ incident level.

We now consider an alternative, more plausible, explanation for the absence of these oscillations for $v_A = 8$ incident levels. Alexander and Corey⁵ showed that four potential energy surfaces are required in the quantum treatment of collision-induced transitions between and within $^2\Pi$ and $^2\Sigma^+$ electronic states. The most important of these surfaces in determining $\Pi \rightarrow \Sigma$ electronically inelastic cross sections is the off-diagonal electrostatic matrix element V_1 between the Σ and $\Pi(A')$ wave functions. While neither of these dynamical limits is valid for thermal energy CN-Ar collisions, it is interesting to note that the $\Pi \rightarrow \Sigma$ cross sections are proportional to matrix elements of V_1 in a total- \mathcal{J} basis both in a perturbative, weak-collision limit (first Born approximation) and in a vibrationally frozen sudden limit.⁵ The even-odd oscillations in the final X state populations can thus be, at least qualitatively, attributed to the near homonuclear dependence of the V_1 surface on the relative atom-molecule orientation angle θ .

For collision-induced transitions between a particular pair of v_A and v_X manifolds, the electronically inelastic cross sections are actually governed by the matrix element $\langle v_A | V_1 | v_X \rangle$ which is an average over the CN vibrational coordinate r . Clearly then, the lack of observable even-odd oscillations in $v_A = 8$ collisions can be related to a vibrational state dependence of the anisotropy of the $\langle v_A | V_1 | v_X \rangle$ ma-

trix elements. Figure 5 displays the dependence of the electronic energy of several states of CN vs internuclear separation. It can be seen that the A and X state electronic energies are nearly degenerate for $v_A = 8/v_X = 12$ (as well as for $v_A = 7/v_X = 11$) at the outer vibrational turning point. The dependence on θ of the off-diagonal electronic matrix element V_1 could likely be significantly different at this internuclear separation than for smaller r , where the electronic energy separation is much larger. Thus, we might reasonably expect a different anisotropy for $\langle v_A | V_1 | v_X \rangle$ for $v_A = 8$ vs $v_A = 3$. Werner and Alexander²⁵ are currently engaged in the *ab initio* calculation of the CN-He interaction potentials. They do find that the diagonal Π and Σ interaction potentials indeed exhibit a significant dependence on r . It will be very interesting to have available *ab initio* information on the dependence of the off-diagonal V_1 diabatic potential energy surface on nuclear geometry to test our supposition about the origin of the quenched even-odd oscillations for $v_A = 8$ collisions.

Since the e and f levels of a given N in the $v_X = 12$ manifold are significantly split in energy because of the $A \sim X$ perturbation, it has been possible to probe separately the populations in these doublets (see the Appendix). We observe here for $v_A = 8 \rightarrow v_X = 12$ collisions a slight but significant preference for population of the final e , rather than f , level in the X state, regardless of the initial A state prepared. It was also possible to separately probe the final e and f level X state populations for high N in $v_A = 7 \rightarrow v_X = 11$ collisions because of the large spin $v_X = 11$ splitting from the $A \sim X$ perturbation.¹ In this case, a small but opposite preference for production of f levels was observed. These results for CN contrast with those reported for N_2^+ $v_A = 4 \rightarrow v_X = 7$ collisions, where significant differences in final e/f populations were observed^{3(b)} as a function of incident A state rotational levels. These variations could be explained by the IOS scaling relations developed by Alexander and Corey⁵ for $\Pi \rightarrow \Sigma$ transitions. For N_2^+ , the e and f rotational lines are resolved

because of the $B \sim A$ perturbation in the upper state. As mentioned earlier, isolated molecule $A \sim X$ mixing is prohibited in this homonuclear ion.

Alexander and Corey⁵ showed that in the high- J Hund's case (b) limit collisional transitions from the $^2\Pi$ state will populate only one spin-doublet level of a given N value in the $^2\Sigma^+$ state. Specifically, e levels are predicted to be exclusively produced from initial F_1 $^2\Pi$ levels, and conversely, f levels from F_2 initial levels. This propensity rule was shown to be consistent with a physical model in which the electron spin S is unaffected by the collision so that the relative orientation of N and S is preserved. Our observations on CN disagree with these predictions. However, all Π state initial levels studied are still fairly close to the case (a) levels limit because of the relatively large ratio $A/B = -30.7$,⁸ so that this propensity rule does not apply to these levels.

We speculate that the preference for production of e levels in the $v_X = 12$ manifold for CN $v_A = 8$ collisions and $v_X = 11$ f levels for $v_A = 7$, at least for high final N values, is related to the larger Π character in these nominally $X^2\Sigma^+$ levels, as compared to their adjacent spin doublets of opposite e/f symmetry. The Π state character in the $v_X = 12$ manifold ranges from 3.7% to 5.5% in the e levels for $N = 0-15$, while the Π admixture is considerably lower in the f levels, varying from 2.9% at $N = 1$ monotonically down to 0.6% at $N = 15$. However, in the $v_X = 11$ manifold, the situation is reversed. The Π state character is highest in the f levels. The $A \sim X$ perturbation reaches a maximum (43.2% Π state character) in the f manifold at the crossing at $N = 14$,⁸ and the state mixing is still 10.2 and 1.7% at $N = 15$ and 20, respectively. By contrast, the Π state character is only 0.3 and 0.8% for the e levels over $N = 0$ to 15. Hence, in both cases ($v_X = 11$ and 12), the larger e/f populations occur for states with the greater Π state admixture.

ACKNOWLEDGMENTS

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APPENDIX: TRANSITION WAVE NUMBERS FOR THE CN $B-A$ (9,8) AND $B-X$ (9,12) BANDS

We present in this appendix the experimentally measured transition wave numbers for the CN $A^2\Pi-X^2\Sigma^+$ (9,8) and $B^2\Sigma^+-X^2\Sigma^+$ (9,12) bands. These data, which are presented in Tables I and II, are included in this paper since these bands have not been previously observed and the spectroscopy of the cyanide radical continues to be of great interest. Moreover, because of the $A \sim X$ perturbation, the

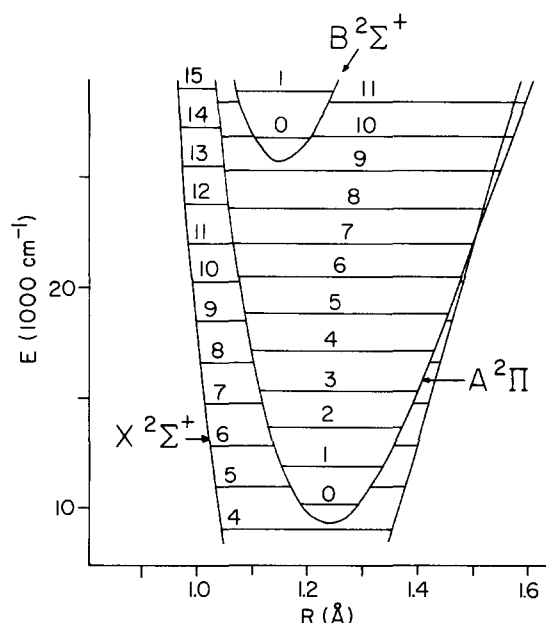


FIG. 5. Potential energy curves and vibrational energies (referred to the bottom of the X state potential) for the low-lying states of the CN molecule.

TABLE I. Observed transition wave numbers^a in the CN $B^2\Sigma^+-A^2\Pi$ (9,8) band.^b

N^c	P_1	Q_1	R_1	Q_2	R_2	P_{12}
1	20 564.42		20 574.02	20 517.92		...
2	20 559.42		20 576.66	20 520.02		
3	20 555.66		20 579.94	20 522.30	20 535.77	20 505.09
4	20 552.35		20 583.56	20 525.02 ^d		20 500.82
5	20 549.41	20 566.70	20 587.47	20 527.76	20 547.80	20 496.77
6	20 546.87	20 567.72	20 591.83	20 530.91 ^d	20 554.30	20 492.99
7	20 544.75	20 568.99	20 596.70	20 534.26	20 560.98	20 489.40
8	20 543.12	20 570.75	20 601.93	20 537.80	20 567.84	20 486.07
9	20 541.65	20 572.87	20 607.59			20 483.02
10	20 540.76	20 575.23	20 613.53	20 545.57		20 480.12
11	20 540.33	20 578.15	20 619.58		20 590.43	20 477.54
12		20 581.43				20 475.32
13		20 585.01				
14		20 589.03				
15		20 593.29				

^a R_{21} and P_2 branches not reported since these lines were weak or overlapped.^b Absolute accuracy of 0.2 cm^{-1} and relative precision of 0.05 cm^{-1} .^c A state rotational angular momentum quantum number.^d Blended line.

(9,12) band is one of the few $B-X$ bands where lines from the e and f spin doublets are resolved. Assignments were made mainly by the use of lower-state combination differences calculated from the analysis of the $A-X$ system by Kotlar *et al.*⁸ Term values for both e and f parity levels in the $B^2\Sigma^+ v = 8$ manifold were also calculated from our reported $B-A$ line positions and A state term values, which can be calculated to relatively high accuracy from the work of Kotlar *et al.*⁸ Spin doubling for $v_A = 8$ is negligible for the N levels observed, as expected from the small values of γ observed for other B state vibrational levels.²⁶ No perturbations are evident, and the term values can be fit to the standard rotational energy formula with $B = 1.7277 \pm 0.0017\text{ cm}^{-1}$; the centrifugal distortion constant could not be determined. The fitted rotational constant agrees well with that reported by Douglas and Routly²⁷ and Schoonveld and Sundaram.²⁸

TABLE II. Observed transition wave numbers in the CN $B^2\Sigma^+-X^2\Sigma^+$ (9,12) band.^a

N^b	P_1	P_2	R_1	R_2
0	20 480.57	...
1	20 473.91	...	20 484.16 ^c	20 484.31 ^c
2	20 470.50	20 470.80	20 487.74	20 488.06
3	20 467.16	20 467.69	20 491.41	20 491.84
4	20 464.12	20 464.70	20 495.27	20 495.83
5	20 461.01	20 461.74	20 499.19	20 499.81
6	20 458.18	20 458.88	20 503.26	20 503.95
7	20 455.41	20 456.29	20 507.36	20 508.17
8	20 452.80	20 453.69	20 511.59	20 512.48
9	20 450.20	20 451.24	20 516.00	20 516.90
10	20 447.86	20 448.77	20 520.50	20 521.47
11	20 445.60	20 446.58	20 525.02 ^c	20 526.01
12	20 443.38	20 444.40	20 529.71	20 530.91 ^c
13	20 441.27	20 442.24		

^a Absolute accuracy of 0.2 cm^{-1} and relative precision of 0.05 cm^{-1} .^b X state rotational angular momentum quantum number.^c Blended line.¹N. Furio, A. Ali, and P. J. Dagdigian, Chem. Phys. Lett. **125**, 561 (1986); J. Chem. Phys. **85**, 3860 (1986).²Guo Jihua, A. Ali, and P. J. Dagdigian, J. Chem. Phys. **85**, 7098 (1986).³(a) D. H. Katayama, J. Chem. Phys. **81**, 3495 (1984); (b) D. H. Katayama and A. V. Dentamaro, *ibid.* **85**, 2595 (1986).⁴D. H. Katayama, Phys. Rev. Lett. **54**, 657 (1985).⁵M. H. Alexander and G. C. Corey, J. Chem. Phys. **84**, 100 (1986).⁶W. M. Gelbart and K. F. Freed, Chem. Phys. Lett. **18**, 470 (1973); K. F. Freed, Adv. Chem. Phys. **42**, 207 (1980).⁷M. H. Alexander, J. Chem. Phys. **76**, 429 (1982); M. H. Alexander and M. Osmolovsky, *ibid.* **77**, 839 (1982); B. Pouilly, J.-M. Robbe, and M. H. Alexander, J. Phys. Chem. **88**, 140 (1984).⁸A. J. Kotlar, R. W. Field, J. I. Steinfeld, and J. A. Coxon, J. Mol. Spectrosc. **80**, 86 (1980).⁹N. Sadeghi and D. W. Setser, Chem. Phys. Lett. **77**, 308 (1981); J. Chem. Phys. **79**, 2710 (1983).¹⁰A. Rotem, I. Nadler, and S. Rosenwaks, Chem. Phys. Lett. **83**, 281 (1981); J. Chem. Phys. **76**, 2109 (1982); A. Rotem and S. Rosenwaks, Opt. Eng. **22**, 564 (1983).¹¹R. F. Heidner, D. G. Sutton, and S. N. Suchard, Chem. Phys. Lett. **37**, 243 (1976).¹²P. Andresen, H. Joswig, H. Pauly, and R. Schinke, J. Chem. Phys. **77**, 2204 (1982); H. Joswig, P. Andresen, and R. Schinke, *ibid.* **85**, 1904 (1986).¹³T. Orlikowski and M. H. Alexander, J. Chem. Phys. **79**, 6006 (1983); G. C. Corey and M. H. Alexander, *ibid.* **85**, 5652 (1986).¹⁴G. C. Nielson, G. A. Parker, and R. T. Pack, J. Chem. Phys. **66**, 1396 (1977).¹⁵See also A. Ali, N. Furio, and P. J. Dagdigian, Chem. Phys. Lett. **136**, 483 (1987).¹⁶S. P. Davis and J. G. Phillips, *The Red System of CN* (University of California, Berkeley, 1963).¹⁷J. B. Halpern and X. Tang, Chem. Phys. Lett. **97**, 170 (1983).¹⁸M. Costes, C. Naulin, and G. Dorthe, Chem. Phys. Lett. **113**, 569 (1985).¹⁹D. C. Cartwright and P. J. Hay, Astrophys. J. **257**, 383 (1982).²⁰M. Larsson, P. E. M. Siegbahn, and H. Ågren, Astrophys. J. **272**, 369 (1983).²¹N. Furio, A. Ali, P. J. Dagdigian, and H.-J. Werner (to be published).²²D. H. Katayama, T. A. Miller, and V. E. Bondybey, J. Chem. Phys. **71**, 1662 (1979).²³B. Pinchemel and P. J. Dagdigian, Chem. Phys. Lett. **106**, 313 (1984).²⁴R. A. Gottscho, R. W. Field, K. A. Dick, and W. Benesch, J. Mol. Spectrosc. **74**, 435 (1979).²⁵H.-J. Werner and M. H. Alexander (work in progress).²⁶R. Engleman, Jr., J. Mol. Spectrosc. **49**, 106 (1974).²⁷A. E. Douglas and P. M. Routly, Astrophys. J. Suppl. **1**, 295 (1955).²⁸L. Schoonveld and S. Sundaram, Astrophys. J. Suppl. **41**, 669 (1979).