

FIG. 2. Series of observed Q-branch transitions with frequencies relative to 10 000.0 MHz. The actual observed line-widths were much smaller than indicated in the above figure.

It appears that no calculations have been done for this complex. Calculations for this complex would be inter-

esting, however, since there are a number of possible binding sites for Ar. Work is continuing on this project.

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## Fluorescence polarization as a probe of molecular autoionization<sup>a)</sup>

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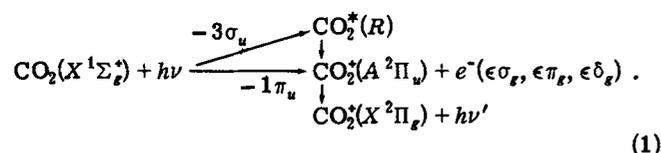
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Extensive effort in VUV spectroscopy has gone into developing an understanding of the spectroscopy and dynamics of autoionizing Rydberg states.<sup>1-6</sup> In this communication, we show that the polarization of fluorescence from excited-state molecular photoions can be a significant tool in ascertaining both the symmetry signature and dynamical properties of autoionizing resonances. The process studied in the present work is given below:



$R$  denotes a Rydberg state;  $-3\sigma_u$  and  $-1\pi_u$  indicate which electron is excited;  $\epsilon$  denotes a continuum electron. The experiment is carried out by scanning the excitation photon energy  $h\nu$  and measuring the polarization of the undispersed  $\text{CO}_2^*(A^2\Pi_u - X^2\Pi_g)$  fluorescence ( $h\nu'$ ).

Previous work has shown that the fluorescence polarization from molecular photoions reflects the degree of alignment of the molecular ion in the laboratory-fixed

frame, which is, in turn determined by the relative dipole strengths for degenerate photoionization channels<sup>7</sup> which have different symmetries in the molecule-fixed frame. The earlier study utilized the fluorescence polarization measurements to gain otherwise experimentally unobtainable information on the ratio of intensities for the degenerate  $\epsilon\sigma_g$  and  $\epsilon\pi_g$  photoelectrons formed by direct (i.e., nonresonant)  $2\sigma_u$  photoionization in  $\text{N}_2$ . Here we use the same framework to infer, from fluorescence polarization measurements, the symmetry properties of autoionizing resonances which are superimposed on a nonresonant background of known symmetry.

The experimental apparatus has been described previously.<sup>7</sup> In this work, monochromatic VUV radiation (0.8 Å bandwidth) from the NBS synchrotron radiation facility (SURF-II) intersected the gas sample which expanded from an effusive jet. Data were taken at 0.2 Å intervals. The polarization of the incident radiation was  $0.70 \pm 0.05$  [ $P_{\text{inc}} \equiv (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ ]. Fluorescence was collected by a planoconvex lens, passed through a polarizer rotated under computer control, and detected

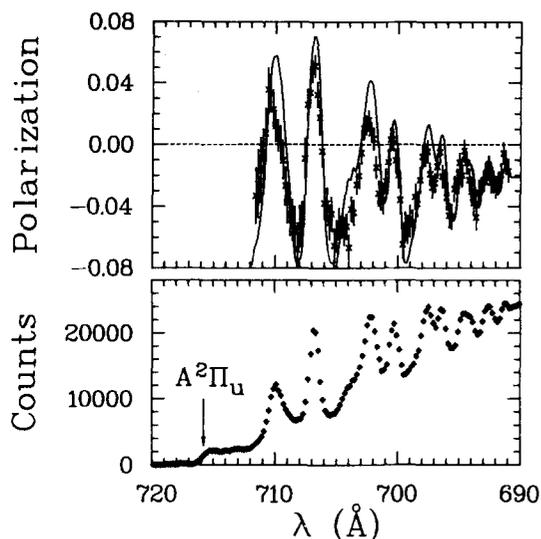


FIG. 1. Bottom frame: fluorescence excitation spectrum for the  $A^2\Pi_u$  state of  $\text{CO}_2^+$ . The threshold is noted by an arrow. Top frame: fluorescence polarization data (corrected) for the  $A^2\Pi_u \rightarrow X^2\Pi_g$  transition of  $\text{CO}_2^+$ , and prediction (solid line) discussed in the text.

by a thermoelectrically cooled photomultiplier tube (RCA C31000A). The results are corrected for photomultiplier tube dark counts, scattered light from the monochromator, solid angle of collection, and partial polarization of the incident radiation. Excitation spectra were recorded with the polarizer removed.

The results are shown in Fig. 1. The excitation spectrum (bottom frame) shows extensive autoionization structure and is in good agreement with results of Gentieu and Mentall<sup>8</sup> and Lee *et al.*<sup>9</sup> The corrected fluorescence polarization data ( $P_{fi}$ , top frame) show structure analogous to the structure in the excitation spectrum, superimposed on a nonresonant background for which  $P_{fi} \sim -0.07$  in regions between well-resolved autoionizing peaks. Theoretical work<sup>10-12</sup> indicates that the  $1\pi_u \rightarrow \epsilon\delta_g$  continuum channel is strongly dominant for several eV above threshold in the absence of autoionization. Hence, for the valleys between the excitation peaks, this implies a nearly pure perpendicular absorption transition; thus, the average angle between the absorption and fluorescence dipoles  $\alpha$  is  $60^\circ$  and  $P_{fi} = -0.077$ ,<sup>7,13</sup> in excellent agreement with the measured value of  $P_{fi} = -0.07 \pm 0.01$ . The autoionization peaks yield polarization values very different from the underlying continuum, owing to the admixture of quasidecrete states with different symmetry. There is some confusion, however, regarding assignments of Rydberg states in this spectral region,<sup>12,14-16</sup> but we will suppose, for the moment, that all of the autoionizing states are of  $1\Sigma_u^+$  symmetry. Thus, the absorption transition is  $1\Sigma_g^+ \rightarrow 1\Sigma_u^+$ , implying  $\alpha = 45^\circ$  and  $P = +0.143$ ,<sup>7</sup> neglecting any change in alignment of the ion due to autoionization.

To test the extent to which this assignment and approximation are realized in this case, we have predicted a polarization spectrum based solely on the excitation spectrum and the previously derived values of  $P_{fi}$

$= -0.077$  and  $P_{fi} = +0.143$  for the nonresonant and resonant intensities, respectively. A simple weighted average was taken at every wavelength: i. e.,  $\bar{r} = (I_{NR}\gamma_{NR} + I_R\gamma_R)/(I_{NR} + I_R)$ , where  $\gamma = (I_{||} - I_{\perp})/(I_{||} + 2I_{\perp})$  is the appropriate polarization index for this averaging procedure. ( $\gamma_{NR} = -0.05$  and  $\gamma_R = +0.10$ ;  $I_{NR}$  and  $I_R$ , the nonresonant and resonant fluorescence intensities, respectively, were determined from the excitation spectrum of Fig. 1.) The resultant  $\bar{r}$  values were transformed back to the  $P_{fi}$  index and are shown in the top frame of Fig. 1 as a solid line. A comparison with the experimental data illustrates that this simple mixing picture accounts for all of the major features. Moreover, this agreement is predicated upon the symmetry designation of  $1\Sigma_u^+$  for the Rydberg features, as a  $1\Pi_u$  designation would result in a flat fluorescence polarization profile with  $P_{fi} = -0.077$ .<sup>13</sup> Hence, these results contradict the earlier assignment<sup>15</sup> of the 707 Å peak as  $1\Pi_u$ .

Note that some discrepancies are observed between the experimental and predicted polarization values. This may indicate the presence of unresolved fine structure due to other Rydberg series, or alternatively, a breakdown of the simple mixing picture employed here. Regarding the latter explanation, the mixing prediction has neglected any change in alignment of the molecular ion due to dynamical effects of autoionization, which may be significant. Specifically, angular momentum may be transferred between the photoelectron and photoion, exerting torque on the molecular ion as the autoionization occurs,<sup>17,18</sup> affecting both the alignment of the excited-state molecular ion and the subsequent fluorescence polarization. Assessment of this effect requires a more comprehensive study than the qualitative discussion presented here. However, the present results and discussion clearly demonstrate that measurements of fluorescence polarization from molecular photoions will yield new insight into spectroscopic and dynamical aspects of molecular autoionization. This has prompted more extensive studies which will be reported in future publications.<sup>13,19</sup>

We wish to acknowledge independent work (J. A. Guest, K. H. Jackson, M. A. O'Halloran, and R. N. Zare; SSRL Activity Report 82/01, May 1982) that also shows autoionization structure in the  $A-X$  fluorescence polarization spectrum of  $\text{CO}_2^+$  in the 700–710 Å excitation wavelength region, corroborating the present observations. We thank Professor Zare for communicating these results to us.

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## Structure of sodium cyanide by molecular beam electric resonance spectroscopy

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Until recently all gaseous alkali metal cyanides<sup>1</sup> were assumed to be linear. Quantum mechanical calculations<sup>2</sup> indicated that this is the case for lithium cyanide. The linear isocyanide configuration LiNC is expected to be the most stable. This structure was indeed deduced from vibrational isotope effects of lithium cyanide in inert gas matrices.<sup>3</sup> Using the same method Ismail *et al.*<sup>4</sup> expected sodium and potassium cyanide to have a linear cyanide configuration. Pietro *et al.*<sup>5</sup> calculated the equilibrium geometry of gaseous KCN using a STO-3G basis set and also found a linear cyanide configuration. Recently gas phase spectroscopy determined accurately and unambiguously the structure of KCN,<sup>6,7</sup> which surprisingly was found to be *T* shaped. In this paper we report the experimentally determined structure of NaCN, which is found to be *T* shaped as well.

A report of the experimentally determined gas phase structure of potassium cyanide<sup>6,7</sup> stimulated *ab initio* potential energy surface calculations on both potassium cyanide<sup>8-10</sup> and sodium cyanide.<sup>9,10</sup> As for LiCN, the M-CN bonding is found to be predominantly ionic: there is an almost complete charge transfer between the CN group and the alkali atom. The potential energy surface in the bending direction has very low barriers for internal rotation (0.3 eV or smaller). This implies that moderate thermal excitation of these molecules is sufficient to allow the M<sup>+</sup> cation to move more or less freely around the CN<sup>-</sup> anion. Clementi *et al.*<sup>2</sup> referred to this as a "polytopic bond," since in this case no structural formula is preferred. However, it is established that both KCN,<sup>6,7</sup> and NaCN (current work) can be considered rigid in the ground vibrational state. Yet the amplitudes of the zero-point bending motion in both molecules can range up to 10°, while for LiCN this amplitude is expected to be even larger.<sup>2</sup>

In this communication we present the results of the first successful observation of the microwave spectrum of sodium cyanide. Earlier attempts by Kuijpers and Törring in our laboratory to observe microwave absorp-

tion of NaCN in the high temperature cell which was used for KCN<sup>11</sup> failed; probably due to polymerization of NaCN in combination with lack of sensitivity. Presently we employed the molecular beam electric resonance technique with essentially the same setup as described before.<sup>6</sup> An argon seeded sodium cyanide beam was used. The temperatures of the supply chamber and the nozzle chamber of the stainless steel oven were typically held at 1100 and 1300 K, respectively. The vapor pressure of NaCN in the supply chamber at this temperature was of the order of 1 mbar, the stagnation pressure of the carrier gas argon was 1 bar. Maintaining a stable beam turned out to be more difficult than for KCN. Clogging occurred after a few hours and before each run the oven had to be cleaned thoroughly. The seeded beam technique was used in order to obtain strong translational, rotational, and vibrational relaxation. Due to the vibrational cooling only transitions of molecules in the ground vibrational state were detected. This simplifies the microwave spectrum and makes identification of the observed transitions feasible. We observed 20 rotational transitions between 9.5 and 40 GHz. The quadrupole hyperfine structure was resolved for most transitions. The linewidth of a single component was about 30 kHz. The signal-to-noise ratio of the strongest lines was 10 using an integration time of 3 s. All the observed rotational transitions were identified as *a*-type (10) and *b*-type (10) transitions of a near-prolate asymmetric top rotor. The observed spectrum

TABLE I. The  $\tau$ -free rotational constants for the ground vibrational state of NaCN.

Constant	Value (MHz)
<i>A</i>	57 920.9(11)
<i>B</i>	8 368.48(17)
<i>C</i>	7 272.37(17)