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## The Electronic Spectrum of Crystalline Bis(diethyldithiocarbamato)nickel(II)

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Polarized crystal spectra reveal four weak absorption bands in the visible region of the spectrum of bis(*N,N*-diethyldithiocarbamato)nickel(II). On the basis of polarization and energy, the transitions involved are assigned as d-d, vibronically induced by a  $b_{2u}$  vibrational mode. The suggested d-orbital ordering is  $d_{xy} > d_{x^2-y^2} > d_{yz} > d_{zx} > d_{z^2}$ . A brief discussion of the vibronic coupling mechanism is given.

Gray and coworkers<sup>1</sup> have made a thorough study of planar complexes in which  $d^8$  metal ions are bound to four sulfur atoms, the latter usually being part of two bidentate chelates of some complexity. Spectral, structural, magnetic, and molecular orbital investigations have led to plausible but unproven ordering schemes for the important molecular orbitals in these complexes. The large number of absorption bands of widely different character that occur in the electronic spectra provide a starting point from which to begin the unraveling of d-d, charge-transfer, and intraligand transitions. Even so, Gray, *et al.*, have identified in their spectra only one or two of the four possible d-d transitions.

One way actually to prove an assignment of an optical spectrum is to obtain crystal spectra and from the polarization behavior and other details to identify the ground and excited electronic states involved. For planar, diamagnetic complexes of  $d^8$  metal ions the ground state is universally accepted as  $^1A_{1g}$ , and hence only the excited electronic states are in need of identification.

The present paper discusses crystal and solution spectra of some disubstituted dithiocarbamato complexes of nickel(II).

## Experimental Section

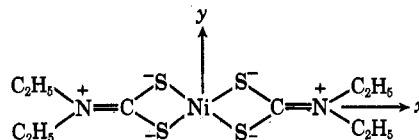
The complexes were prepared after the general method outlined by Cambi and Cagnasso.<sup>2</sup> They were recrystallized from chloroform, benzene, or acetone, chemically analyzed, and oriented by X-ray methods. The crystals of the nickel complexes are dark green or black to the eye, but when thin sections are viewed in polarized light, they are bright green and orange in the two directions of extinction. Two Ni(II) complexes have been studied in some detail; they are bis(*N,N*-diethyldithiocarbamato)nickel(II) [hereafter Ni(DEDTC)<sub>2</sub>] for which a complete crystal structural analysis is available and bis(*N,N*-dipropyldithiocarbamato)nickel(II) for which there are no crystallographic details available. Both crystals give very similar spectra.

Solution spectra have been obtained in a variety of spectroscopic grade solvents using a Cary 14 spectrophotometer. Crystal spectra have been obtained using a microcrystal spectrometer attachment<sup>3</sup> in conjunction with a Cary 14. All crystal spectra were obtained at room temperature.

The Structure of Ni(DEDTC)<sub>2</sub>

The crystal structure of the stable  $\alpha$  form of this

complex has been determined by Shugam and Levina<sup>4</sup> and by Bonamico, Dessy, Mariani, Vaciego, and Zambonelli.<sup>5</sup> The crystals are monoclinic, space group  $P2_1/c$  with the following unit cell dimensions:  $a = 6.19 \text{ \AA}$ ,  $b = 11.54 \text{ \AA}$ ,  $c = 11.60 \text{ \AA}$ ,  $\beta = 95^\circ 51'$ , and  $z = 2$ . The molecular units are planar and the molecular symmetry is  $D_{2h}$ . From crystallographic and ir<sup>6</sup> evidence an important canonical form is



The crystals grown in the present study were very often twinned, and good, thin single crystals were hard to find. Those that were used usually had {011} developed and they showed oblique extinction. Following the crystal structure, it is possible to project the molecules upon this face in order to establish the projections that the molecular axes make on the crystal extinction directions. The resultant absorption intensities with the molecular axes located as shown above are as follows:  $x$  polarized, green/orange,  $\sim 10.0$ ;  $y$ , green/orange,  $\sim 0.3$ ;  $z$ , green/orange,  $\sim < 0.1$ .

## Results

In the visible region, the crystal spectra taken in unpolarized light are very similar to the solution spectra obtained in a variety of solvents. This observation suggests an intramolecular origin for the spectrum.

**Solution Spectra.**—Spectra of planar nickel(II) complexes involving four Ni-S bonds appear to be unaffected by changes in solvent coordinating power.<sup>1,7</sup> This is also the case in the present investigation (Figure 1). (A basis for this behavior will be given after the details of the spectrum have been discussed.) Another feature of Ni-S<sub>4</sub> systems is the high intensity of the absorption bands in the spectrum, the weakest in the present case having  $\epsilon 70 \text{ l. mol}^{-1} \text{ cm}^{-1}$ , very large for a nickel(II) system with a center of symmetry. Shupack, *et al.*,<sup>1</sup> have proposed very strong  $\pi$  and  $\sigma$  bonding in similar complexes, with an attendant breakdown of the 3d character of the orbitals containing the most loosely bound electrons. Thus the d-d forbiddenness of the low-energy transitions is partially

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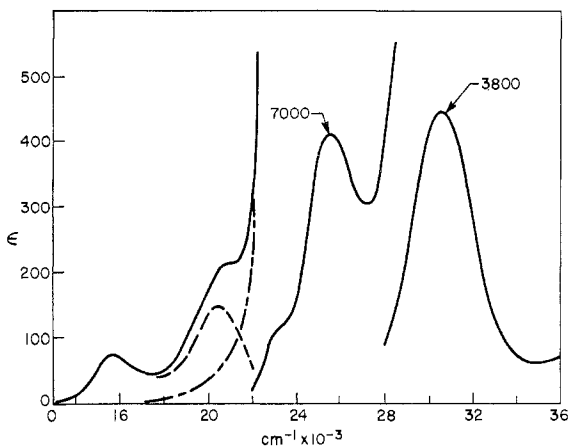


Figure 1.—The spectrum of Ni(DEDTC)<sub>2</sub> in chloroform. Solution spectra taken in pyridine, piperidine, and other strongly coordinating solvents are indistinguishable from that taken in chloroform.

removed, leading to increased absorption coefficients in the low-energy spectrum. Moreover, the proximity of intense absorption bands in the near-uv region serves to exaggerate such increases.

The three features below 25,000 cm<sup>-1</sup> in the solution spectrum (Figure 1) are termed “weak” within our framework, and hence they should correspond to d-d transitions and/or forbidden charge-transfer processes. It is important to point out that there is no simple way unequivocally to distinguish between these two possibilities. Nevertheless, we begin by arguing that the lowest lying band is due to the excitation (Figure 2a)

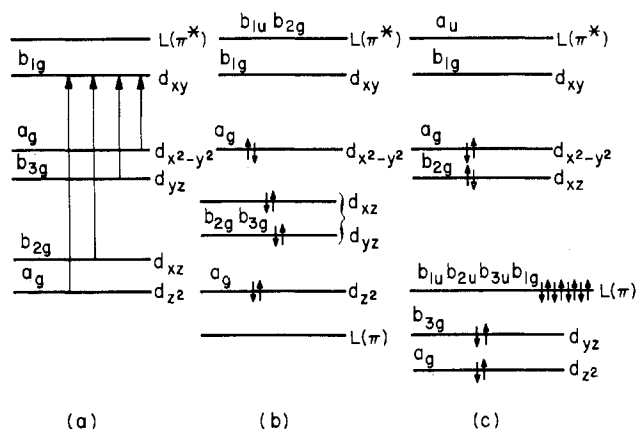


Figure 2.—Three energy level schemes for planar NiS<sub>4</sub> complexes. (a) is that derived in this study from solution and crystal spectral measurements, (b) is that proposed by Latham, Hascall, and Gray<sup>1</sup> for the dithiooxalate complex of nickel(II), and (c) is that proposed by Shupack, *et al.*, for the maleonitriledithiolate complex of nickel(II). Only the ordering of the levels is significant; the vertical energy scale is arbitrary.

$d_{x^2-y^2} \rightarrow d_{xy}$  [ $\nu_{\max}$  15,750 cm<sup>-1</sup>;  $\epsilon$  70 l. mol<sup>-1</sup> cm<sup>-1</sup>]. This assertion is in line with most models for planar d<sup>8</sup> systems. It agrees with the calculated MO scheme of Shupack, *et al.*,<sup>1</sup> and it is only this in-plane transition that should be immune to variations in the axial perturbation provided by solvents of different coordinating power. The other d-d transitions (that are sensitive to axial fields) must be contained in the rapidly increasing absorption that sets in at  $\sim 18,000$  cm<sup>-1</sup>. The shoulder at  $\sim 20,500$  cm<sup>-1</sup> ( $\epsilon \sim 100$  l. mol<sup>-1</sup> cm<sup>-1</sup>,

when the background is subtracted) is attributed to one such process.

In order to deal with the stronger bands that appear at 25,600 cm<sup>-1</sup> and above, we first mention that if the spectrum is shifted some 4000 cm<sup>-1</sup> to lower energy, the five lower energy bands are almost identical in position and relative intensity with those reported by Shupack, *et al.*,<sup>1</sup> in the spectrum of the maleonitriledithiolate-nickel(II) complex (MNT)<sub>2</sub>Ni<sup>2+</sup>. Hence, in view of the expected similarities between these systems, we feel quite justified in using the MO scheme calculated for (MNT)<sub>2</sub>Ni<sup>2+</sup> for the assignment of the low-energy spectrum of Ni(DEDTC)<sub>2</sub>. In that scheme (Figure 2c) the orbital immediately above the vacant  $d_{xy}$  orbital is an antibonding  $\pi^*$  orbital of the ligand with symmetry  $a_u$  (in  $D_{2h}$ ).<sup>8</sup> The shoulder found at  $\sim 23,000$  cm<sup>-1</sup> (Figure 1) is thought to be “metal to ligand” in character and is associated with the orbitally forbidden transition  $d_{x^2-y^2} \rightarrow \pi^*a_u$ . The intense band at 25,600 cm<sup>-1</sup> is also “metal to ligand” and is attributed to the orbitally allowed transitions  $d_{xz,yz} \rightarrow \pi^*a_u$ . These proposals are quite consistent with those advanced by Shupack, *et al.*, for (MNT)<sub>2</sub>Ni<sup>2+</sup>.<sup>9</sup>

**Crystal Spectra.**—In the region below 23,000 cm<sup>-1</sup> the crystal spectrum is very anisotropic. (Unpolarized, the spectrum is similar to the spectrum taken in solution.) There are two types of crystal spectrum depending upon which crystal face is examined (Figures 3, 4). Combining these results it is seen that there are four absorption bands below 22,000 cm<sup>-1</sup>, whereas the solution spectrum shows only two. (Presumably, the same is true of crystals containing (MNT)<sub>2</sub>Ni<sup>2+</sup>.) Here, we propose that these new, weak bands are the “missing” d-d transitions. Since this means that there are 4 d-d transitions,<sup>11</sup> the true  $D_{2h}$  molecular symmetry should be appropriate for the analysis.

A vibronic coupling mechanism must be introduced in order to combat the parity restriction in this  $D_{2h}$  system. Because the spectra are so anisotropic, because the  $D_{2h}$  symmetry group contains only onefold orbitally degenerate representations, and because each absorption band appears to be polarized in only one molecular direction, it is possible to propose a vibronic model

(8) One might equally justifiably use the MO scheme given by Latham, Hascall, and Gray.<sup>1</sup> Indeed, the same overall result will obtain but with the added advantage that the  $L(\pi)$  orbitals lie deeper than the d antibonding set. (See Figure 2b.)

(9) Although it is not the purpose of this paper to discuss the intense uv spectra of these compounds, the following brief comments certainly appear relevant. Various salts of the ligand DEDTC dissolved in polar solvents such as H<sub>2</sub>O, ethanol, etc., give uv spectra that show three strong bands (34,500, 38,800, and 48,500 cm<sup>-1</sup>) as well as a weak, solvent-sensitive band at  $\sim 28,000$  cm<sup>-1</sup>. We do not propose to give assignments for these transitions, although it seems reasonable to label them  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*(2)$ , and  $\sigma \rightarrow \sigma^*$  in order of increasing energy. The point of this footnote is to emphasize the fact that Ni(DEDTC)<sub>2</sub> has only two strong uv transitions (at 31,000 and 40,500 cm<sup>-1</sup>), neither of which falls at a free-ligand position. Similar observations have been made in the spectrum of nickel(II) complexes of *N,N*-diethylidisenocarbamates.<sup>7</sup> Clearly, correlations in complex spectra between unperturbed ligand spectra and those in complexes need to be made cautiously. If we assume the bands at 31,000 and 40,500 cm<sup>-1</sup> are perturbed ligand transitions, the high-energy  $L \rightarrow M$  transitions (as seen in (MNT)<sub>2</sub>Ni<sup>2+</sup>) must lie exactly under the  $L \rightarrow L$  transitions. Since this is unlikely, we propose that for Ni(DEDTC)<sub>2</sub> the  $L(\pi)$  orbitals should lie deeper in energy than in (MNT)<sub>2</sub>Ni. (See Figure 2b.)

(10) Because of the rapidly increasing absorption coefficient we have been unable to make measurements above this energy.

(11) It has been pointed out by a referee that the presence of four absorption bands does not necessarily mean that there are four independent electronic transitions involved. While in principle this is true, we follow many earlier works in assuming that bands separated by  $>1000$  cm<sup>-1</sup> are indeed separate electronic transitions.

that requires only one odd vibrational mode. The resultant crystal energy level scheme is compatible with that derived from the solution results.

The lowest transition ( $\nu_{\max}$  15,900  $\text{cm}^{-1}$ ) is assigned to the excitation  $d_{x^2-y^2} \rightarrow d_{xy}$ , and in the present coordinate system this transition is  ${}^1A_{1g} \rightarrow {}^1,{}^3B_{1g}$ . Neglecting the triplet and noting that the polarization of this band is  $x$  (Figures 3, 4), the only odd vibration that can be active is  $b_{2u}$ . Furthermore, the excitation  $d_{z^2} \rightarrow d_{xy}$  has the same symmetry properties as the above transition, and it will also be  $x$  polarized if only a  $b_{2u}$  vibration is effective. The strongly  $x$ -polarized shoulder at 21,000  $\text{cm}^{-1}$  (Figures 3, 4) is assigned to

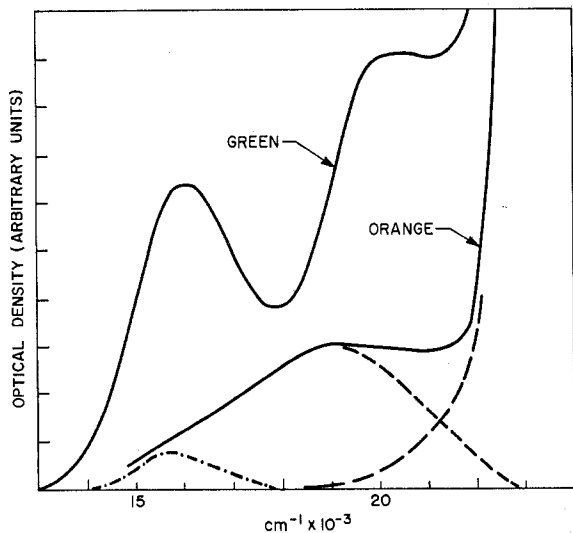


Figure 3.—Polarized single-crystal spectrum of Ni(DEDTC)<sub>2</sub> taken on the (011) crystal face.

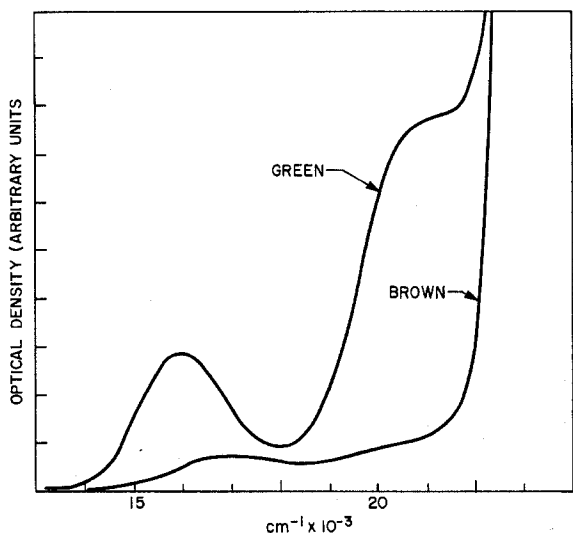


Figure 4.—Polarized single-crystal spectrum of Ni(DEDTC)<sub>2</sub> taken on an unknown crystal face that is approximately normal to (011). The absence of the 19,000- $\text{cm}^{-1}$  band from the brown spectrum indicates that the brown spectrum is essentially that for  $y$  polarization. The green spectrum is  $x$  polarized as in Figure 3.

this latter excitation, an association which is fitting, since  $d_{z^2} \rightarrow d_{xy}$  should be the highest energy d-d transition (Figure 2).

Between these two  $x$ -polarized absorptions there are two weaker bands. The  $z$ -polarized band at 19,000

$\text{cm}^{-1}$  is assigned to the transition  ${}^1A_{1g} \rightarrow {}^1B_{3g}$  ( $d_{zz} \rightarrow d_{xy}$ ) which must be coupled to a  $b_{2u}$  vibration in order to give the observed polarization. The weaker, less strongly polarized band at 17,000  $\text{cm}^{-1}$  is associated with  ${}^1A_{1g} \rightarrow {}^1B_{2g}$  ( $d_{yz} \rightarrow d_{xy}$ ). This transition remains forbidden even after the intervention of a  $b_{2u}$  vibration. The fact that it is much weaker than the other d-d transitions is interpreted to mean that vibrations other than  $b_{2u}$  are not effective in introducing intensity into the d-d transitions. Indeed, if they had been, the transitions at 15,900 and 21,000  $\text{cm}^{-1}$  would have been much less strongly polarized. Moreover, the fact that the strong transition(s) at 23,000  $\text{cm}^{-1}$  and above has (have) considerable intensity in all  $x$ ,  $y$ , and  $z$  orientations (Figures 3, 4) assures one that if other vibrations were active, bands of mixed polarization would appear in the low-energy spectrum.

The above assignments lead to an energy level scheme as shown in Figure 2a. Although this d-orbital ordering is very reasonable, it is not unique, since it depends upon our initial choice of lowest excited state. The spectra obtained from bis(*N,N*-dipropylthiocarbamate)nickel(II) are very similar to those in Figures 3 and 4, and presumably they arise in the same manner.

#### Discussion

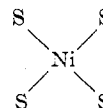
Without being unreasonably optimistic, we believe that the collected evidence supports the proposal that the four low-energy features in the crystal spectra are d-d in origin. If some of these bands were vibronically induced charge-transfer transitions, it would be unlikely that a reasonable ordering of d orbitals would result. Nevertheless, we have not *proven* that the transitions are d-d; only the symmetry properties of the excited vibronic states and the symmetry of the coupled odd vibration have been established by our treatment.

Assuming the excitations to be d-d, the d-orbital level scheme is  $d_{xy} > d_{x^2-y^2} > d_{yz} > d_{zz} > d_{z^2}$ . This agrees with that calculated in ref 1 except for the reversal of  $d_{zz}$  and  $d_{yz}$ . This difference does not seriously question the general validity of the Shupack, *et al.*,<sup>1</sup> calculation.

Conversely, one might question the validity of an energy level scheme that has been derived from a vibronic coupling analysis, especially when only one odd vibrational symmetry has been invoked. We qualify the details of the analysis in the following way. First, the choice of  $d_{x^2-y^2} \rightarrow d_{xy}$  as the lowest energy transition is consistent with practically all published energy level schemes for planar Ni(II) systems as well as with qualitative models that one might propose. Second, the presence of allowed intensity in *all*  $x$ ,  $y$ , and  $z$  directions at  $\geq 23,000$   $\text{cm}^{-1}$  (assuming equal vibronic matrix elements between these essentially equienergetic excited states and those below 23,000  $\text{cm}^{-1}$ ) means that vibronic intensity may be induced in  $x$ ,  $y$ , and  $z$  directions in the d-d spectra. Finally, the fact that intensity appears in only one molecular direction (excluding the very weak  $d_{yz} \rightarrow d_{xy}$  excitation) for any given d-d transition can only be interpreted to mean that for a given transition only one vibrational mode is active. That only one vibrational symmetry,  $b_{2u}$ , is needed for the analysis is based in part upon our initial choice for the lowest energy transition. As we have mentioned before, the resultant d-orbital ordering is reasonable but not unique.

The observation that only one odd vibrational mode is necessary to explain the polarizations and intensities is very interesting. (The very weak  $\sim 17,000\text{-cm}^{-1}$  band, forbidden in this limit, obviously does not gain much intensity from any other vibrational mode.) Indeed, the simplicity of this vibronic coupling scheme is very unusual. In the past,<sup>12-18</sup> spectra of such complex nuclear systems have generally required several vibrational symmetries to be introduced, and ambiguous situations resulted.<sup>12-15</sup> It is not clear why similar problems do not arise in the present case. What is

known, however, is that in a five-atom model



there are two  $b_{2u}$  vibrations ( $D_{2h}$ ) and they are both derived from the  $e_u$  modes of  $D_{4h}$ . These latter modes have been shown to be important in vibronically induced transitions in  $D_{4h}$  (or nearly  $D_{4h}$ ) systems.<sup>16</sup>

Further speculation about the source of the vibronic intensity is not warranted. If more information could be obtained (from vibronic spectra at low temperatures for instance), it could lead to a better understanding of the complicated problem of vibronic processes in metal chelates.

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## Microwave Spectrum, Structure, and Dipole Moment of 2-Carbaheborane(9), $\text{CB}_5\text{H}_9$ <sup>1</sup>

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The microwave spectrum of 2-carbaheborane(9) has been studied in the region of 8–37 GHz. The rotational spectra of the normal species (all <sup>11</sup>B isotope) and seven <sup>10</sup>B-substituted species were assigned. The principal axis coordinates of the boron atoms were calculated from the moments of inertia of the normal species and of the three singly substituted <sup>10</sup>B species. The results show that the main framework is a pentagonal pyramid. The following bond lengths were accurately determined:  $r_{\text{B}(3)-\text{B}(4)} = 1.759 \text{ \AA}$ ,  $r_{\text{B}(4)-\text{B}(5)} = 1.830 \text{ \AA}$ ,  $r_{\text{B}(1)-\text{B}(2)} = 1.782 \text{ \AA}$ , and  $r_{\text{B}(1)-\text{B}(4)} = 1.781 \text{ \AA}$ . The Stark effect of the normal species and of two singly substituted B(10) species was measured. The molecular dipole moment was found to be  $1.53 \pm 0.03 \text{ D}$ .

### Introduction

The preparation of a new carborane with the empirical formula  $\text{CB}_5\text{H}_9$  has been reported by Dunks and Hawthorne.<sup>4</sup> From the analysis of the <sup>11</sup>B nmr spectrum and the proton nmr spectrum the authors concluded that the molecule has two pairs of equivalent boron atoms, three bridge hydrogen atoms, and a boron atom at an apical position. The spectrum is consistent with the pentagonal pyramid shown in Figure 1.

Since a molecule with this geometry must have a nonvanishing dipole moment, the pure rotational spectrum should be observable. The microwave spectrum of a sample of naturally abundant isotopic species was investigated to determine the coordinates of the boron atoms and the dipole moment.

### Experimental Section

The sample of  $\text{CB}_5\text{H}_9$  was kindly provided by Dunks and Hawthorne. The original sample, after taking the <sup>11</sup>B nmr spectrum, had been kept in a sealed nmr tube at room temperature for several months. It was purified by fractionation before use in our microwave study. No impurity problem nor decomposition of the sample was encountered in the study of the rotational spectrum.

The microwave spectrum between 8.2 and 37.5 GHz was observed with a conventional 100-kHz Stark modulated spectrometer. Frequencies were measured by interpolating between standard frequencies with a Collins Model 51S-1 receiver. The standard frequencies were obtained by multiplying the output of a 1-MHz crystal in a Hewlett-Packard Model 5245L frequency counter with General Radio standard frequency multipliers. The uncertainties of the measured frequencies were generally less than  $\pm 0.1 \text{ MHz}$ .

The spectrum was studied at Dry Ice temperature and at pressures between 10 and 40  $\mu$ . For better resolution, certain stronger lines were measured at pressures below 2  $\mu$ .

Dc biasing of the 100-kHz square wave was used to measure the Stark effects. The electric field calibration of the Stark cell was made with the  $J = 1 \leftarrow 0$  transition of carbonyl sulfide.<sup>5</sup> All dipole moment measurements were performed the same day.

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