

# Electron diffraction studies of laser-pumped molecules. II. Collisionally assisted absorption by SF<sub>6</sub>

L. S. Bartell, M. A. Kacner, and S. R. Goates

*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109*  
(Received 27 April 1981; accepted 12 June 1981)

Supersonic microjets of SF<sub>6</sub> were pumped with the cw output of a CO<sub>2</sub> laser. Power densities ranged from 2–4 kW/cm<sup>2</sup> at the nozzle exit ( $P \leq 200$  Torr) to 25 kW/cm<sup>2</sup> downstream. Amplitudes of molecular vibration were found to increase significantly when the laser was tuned to the  $\nu_3$  resonance and even a slight expansion of bond lengths was observed. Up to two photons per molecule were absorbed at the higher nozzle pressures. At such pressures the maximum response was red shifted from that of the 300 K optical absorption band. Electron diffraction patterns taken a microsecond after excitation showed virtually complete  $V-V$  relaxation. Because little  $V-T$  relaxation took place in the jet expansion, the translational temperature downstream fell to 20 K while vibrational temperatures remained hot, at perhaps 500 K. The correspondence between the pumping of supersonic jets and the irradiation of static systems is briefly discussed.

## I. INTRODUCTION

Physical and chemical processes initiated by the absorption of radiation have been studied for many decades. A rapid increase of activity in this area followed the discovery that lasers can stimulate certain molecular systems to a high degree of vibrational excitation and induce potentially valuable reactions.<sup>1-4</sup> Most such studies have been carried out on static systems of molecules and followed spectroscopically by absorption, photoacoustic, double resonance, or infrared fluorescence techniques, or followed chemically. An alternative approach has begun to be explored, namely the investigation of pumped supersonic jets. An important study making use of bolometric measurements appeared recently.<sup>5</sup> For a review of the special advantages offered by supersonic jets we refer to that work. The probing of pumped jets by electron diffraction techniques offers another means of measurement which we hereby examine. Preliminary studies<sup>6-8</sup> have confirmed that electron diffraction can detect vibrational excitation in favorable cases despite its limited sensitivity. In comparison with spectroscopic techniques capable of characterizing sparsely populated states in detail, electron diffraction reveals only certain molecular properties averaged over the entire ensemble probed. Nevertheless, electron diffraction possesses enough potentially attractive features to warrant careful consideration.

These features are most easily understood by reviewing the principles involved.<sup>9</sup> Each internuclear distance in a gas-phase molecule is registered in an electron diffraction pattern as a set of concentric sinusoidal interference fringes whose rate of damping provides a sensitive measure of the amplitude of vibration of the (bonded or nonbonded) atom pair. Therefore, changes in the diffraction pattern signify how much vibrational excitation has been imparted to each atom pair. Whereas absorption spectroscopy may show sensitively how many quanta have been absorbed by an ensemble of molecules, it does not follow the course of the excitation. By contrast, electron diffraction can show, at a given time, how many quanta have been retained as vibrational energy, whether this energy has remained in the mode pumped or whether it has been redistributed over many modes, what the character of the redistribution is,

whether the energy is concentrated in a fraction of the molecules or is uniformly distributed over the ensemble, and what fraction of the energy absorbed has flowed into translational velocity. The time between irradiation and measurement can be readily controlled from 1 to 20  $\mu$ s. With special techniques the time range could be extended. Although large molecules relax much more rapidly than this, it is not clear that all lightly pumped small molecules do. Arvedson and Kohl obtained preliminary evidence that SF<sub>6</sub>, in fact, does not.<sup>6,7</sup>

The favorable aspects of electron diffraction stem from the fact that it monitors quite directly the internal mechanics of vibrating molecules. Unfortunately, the signal observed cannot be selected to be that of the excited subset of molecules; the signal collected is that of the entire ensemble. Therefore, the fraction of molecules excited must be considerable in order for the signal registering excitation to be extracted from the signal associated with the substantial thermal agitation of unpumped molecules. Whether the excitation attainable is enough for useful information to be derived by electron diffraction is investigated in the following.

## II. EXPERIMENTAL

### A. Apparatus and conditions

The principal features of the system comprising a tuneable cw CO<sub>2</sub> laser and a gas-phase electron diffraction unit are outlined in paper I.<sup>10</sup> Laser powers ranging from 20 to 40 W and lines from 932 to 1050 cm<sup>-1</sup> were employed to irradiate jets of SF<sub>6</sub> vapor issuing from a stainless steel nozzle 0.12 mm in diameter and 4 mm long. Stagnation pressures from 50 to 600 Torr were controlled by adjusting the temperature of the condensed substance while monitoring pressure with a mercury manometer. The focused laser spot (Gaussian,  $\sigma \approx 0.15$  mm) was centered 0.3 to 0.35 mm from the nozzle tip. In runs with SF<sub>6</sub> pressures below 300 Torr, the center line of the 40 kV electron beam (radius  $\approx 0.2$  mm at gas jet) passed 0.62 to 0.66 mm from the nozzle tip. At higher pressures the spacing was reduced to 0.52 mm. Electron diffraction exposures, taken with a beam current of about 0.7  $\mu$ A, decreased from about 10 to 0.7 s as gas pressure increased. Diffraction patterns were

filtered through an  $r^3$  rotating sector of 48 mm radius in all runs and recorded from  $3.7 < s < 21.3 \text{ \AA}^{-1}$  on 4 in.  $\times$  5 in. Kodak electron image plates. Sulfur hexafluoride with a stated purity of 99.99% was purchased from the M. G. Scientific Co. for the experiments.

From a total of 205 diffraction plates, 128 were found to be sufficiently flawless for final analyses, including the 41 "control plates" (without irradiation) discussed in paper I.<sup>10</sup> Control plates were always taken at the end of each set of five exposures the first four of which consisted of a 90 s blank (laser on but no sample) followed by three exposures of the irradiated sample.

## B. Analysis of data

Amplitudes of vibration  $l_{ij}$  and mean internuclear distances  $r_{ij}$  were determined from diffraction patterns by conventional least squares procedures<sup>9,11</sup> after the corrections for intramolecular multiple scattering and systematic mean residuals had been made, as described in paper I. Elastic scattering factors were taken from the revised tabulation of Schafer, Yates, and Bonham<sup>12</sup>; inelastic factors were Tavad's.<sup>13</sup> Temperature-dependent Morse parameters  $a(T)$  were calculated as described elsewhere.<sup>14</sup> Internuclear distances (SF,  $FF_{cis}$ , and  $FF_{trans}$ ) in laser-pumped molecules were refined without the imposition of geometric constraints because the harmonic "shrinkage corrections" conventionally introduced together with geometric constraints have not been demonstrated to be adequate for vibrationally excited molecules.<sup>15,16</sup>

Of principal concern in this study, of course, were the amplitudes of vibration. Several different ways of assessing uncertainties in amplitudes were suggested by these data. First, once the reproducible systematic mean residuals had been subtracted from intensities, the residuals from the least squares analyses of individual diffraction plates became essentially random. Error matrices derived from these residuals yielded standard deviations of vibrational amplitudes of individual plates. These standard deviations  $\sigma_{ls}$  are not measures of absolute accuracy but of precision, or sensitivity to changes in conditions. A second measure, derived from the reproducibility itself, or

$$\sigma_{rep} = \left| \sum_{i=1}^N (l_i^2 - \bar{l}^2) / (N-1) \right|^{1/2}, \quad (1)$$

was also available. Usually, three or four plates were taken at a given pressure, laser power, and frequency and hence allowed a reasonable check.

## C. Number of photons absorbed

Kelley and Fink<sup>15</sup> have confirmed that the temperature variation of mean amplitudes in  $SF_6$  follows quite faithfully up to 500 K that calculated from normal coordinate theory based on a spectroscopic quadratic force field. Their absolute amplitudes were offset by a fixed amount from the calculated amplitudes, as were ours also, but the Kelley and Fink offsets were somewhat smaller because their scattering data avoided the smaller angles and the associated systematic residuals discussed in paper I.<sup>10</sup>

By comparing the mean amplitudes  $l_{ij}$  each corrected by an appropriate offset, with temperature dependent calculated amplitudes  $l_{ij}(T)$  we were able to assign a vibrational temperature to each internuclear distance. To characterize the vibrational excitation of a given diffraction pattern, we chose the temperature corresponding to the  $FF_{cis}$  distance because it gave the greatest sensitivity. Because our data were compatible with a Boltzmann distribution of vibrational energy, we used the vibrational heat capacity<sup>17</sup>  $C_{vibr}(T) = C_p(T) - 4R$  to deduce the mean increase in molecular energy from the temperature increase. This increase  $\Delta E = \langle n \rangle h\nu$  leads directly to a measure of  $\langle n \rangle$ , the average number of photons absorbed per molecule and retained as vibrational energy.

## III. RESULTS

### A. Laser-induced changes in molecular parameters

The derived quantities of greatest importance in the present study of infrared pumping are the mean amplitudes of vibration of the irradiated molecules. As explained in paper I,<sup>10</sup> systematic errors in the range of electron scattering angles investigated prevented the determination of absolute amplitude with high accuracy but interfered very little with the measurement of *changes* in amplitudes. Our experimental amplitudes  $l_{ij}$  of unexcited molecules differ by perhaps 0.002 Å (several percent) from calculated values based on spectroscopic frequencies,<sup>18</sup> and the exact value of this systematic offset depends upon the scattering angle inside of which we terminate the data. Therefore we report our results in terms of the *increase* in rms amplitudes or, sometimes, mean-square amplitudes. Our sensitivity is an order of magnitude higher than the absolute accuracy in amplitude.

Of the three kinds of internuclear distance in  $SF_6$ , namely SF,  $FF_{trans}$ , and  $FF_{cis}$ , the latter shows the greatest response to  $CO_2$  laser irradiation, at least in the range of pressure and fluence where absorption is strongly mediated by collisions. Figure 1 shows how the change in the  $FF_{cis}$  amplitude  $\Delta l_{FFc}$  increases with the throughput of effluent  $SF_6$  from the nozzle. Figures 2 and 3 clearly demonstrate molecular changes associated with the direct absorption of quanta into the  $\nu_3$  vibrational mode. In these figures the molecular responses can be seen to parallel, approximately, the infrared absorption spectrum of  $SF_6$  at a somewhat elevated temperature.<sup>19</sup> It is immediately apparent from the observed apportionment of vibrational excitation among the various atomic pairs, however (for example, in Figs. 2 and 4), that the vibrational energy absorbed does not remain localized in the pumped  $\nu_3$  mode. Instead, in the microsecond between the exposure to radiation and the probing by electron diffraction, the vibrational energy becomes quite thoroughly distributed among the various modes.<sup>20</sup>

That the relaxation effecting this redistribution is restricted to  $V-V$  processes and not to a more general equilibration also involving  $V-T$  relaxation is demonstrated by the intensities of scattered electrons. As will be discussed in Sec. III B (in connection with Fig. 6), scattered intensities are not diminished by the ab-

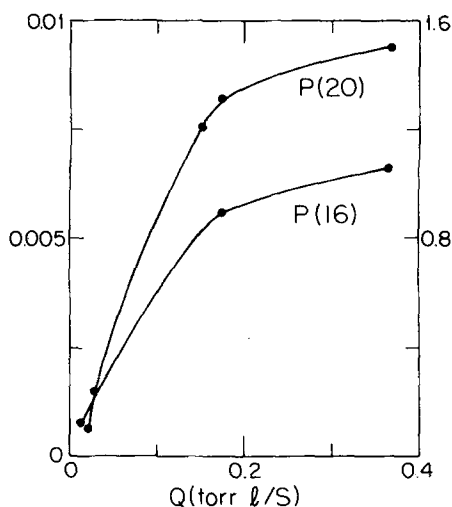


FIG. 1. Excitation of  $\text{SF}_6$  as a function of throughput from the 0.012 cm nozzle, for P(16) and P(20) lines. Left-hand scale, increase in  $\text{FF}_{\text{cis}}$  amplitude of vibration, in Å. Right-hand scale,  $\langle n \rangle$ , the mean number of photons absorbed per molecule. At the highest throughputs, the radiation incident upon the jet streamlines probed by the electron beam has been appreciably attenuated by absorption by outer streamlines. Power density at nozzle tip is about  $2 \text{ kW/cm}^2$ .

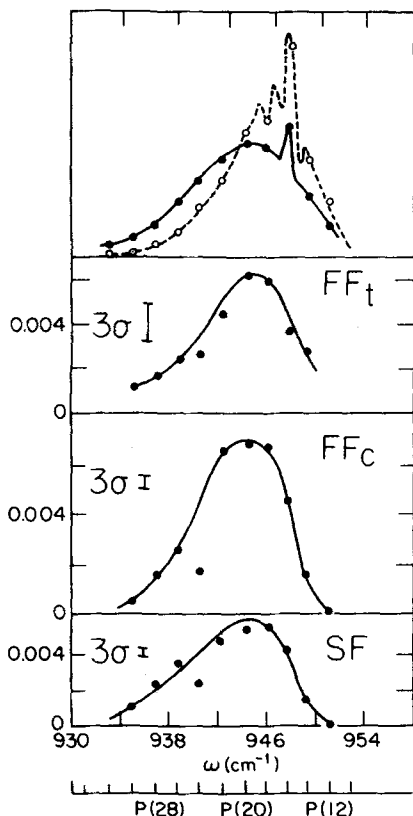


FIG. 2. The three lowest curves represent the observed excitation of  $\text{SF}_6$  as a function of incident laser frequency. Plotted are the increases in rms amplitudes (in Å) of the indicated atom pairs. Experimental conditions,  $P=300$  Torr (stagnation chamber) or  $\approx 100$  Torr (at nozzle exit) and  $W \approx 2 \text{ kW/cm}^2$  at the nozzle tip. Error bars show representative uncertainties  $3\sigma_{\text{LS}}$  for the four-plate averages plotted (see the text). The top curves are optical cross sections of 300 K (dashed) and 400 K (solid) according to Nowak and Lyman (Ref. 19).

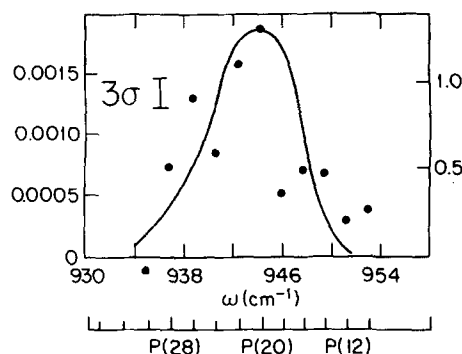


FIG. 3. Points, observed optically induced thermal expansion of mean SF bond length in  $\text{SF}_6$  (left-hand scale, in Å) as a function of incident laser frequency; curve (right-hand scale) is the corresponding mean number of photons absorbed per molecule as inferred from  $\text{FF}_{\text{cis}}$  results in Fig. 2. Conditions are those of Fig. 2.

sorption of infrared radiation by the gas as they would have been if the translational velocity of molecules had increased. Therefore, to within perhaps  $25^\circ$  (12% of the increase in vibrational temperature)  $V-T$  relaxation can be disregarded.

In addition to studying excitation as a function of vapor density and infrared frequency, we also investigated the effect of varying laser power from 21 to 36 W at a fixed sample stagnation pressure of 600 Torr. Unfortunately, certain experimental troubles were encountered in these particular runs that interfered with the reproducibility of configuration. No increase in response with power was observed. Whether this indicates a true saturation or is an artifact is not known. A proposed model of laser excitation predicts no such saturation.<sup>8</sup>

One curious effect related to pumping was seen. Or-

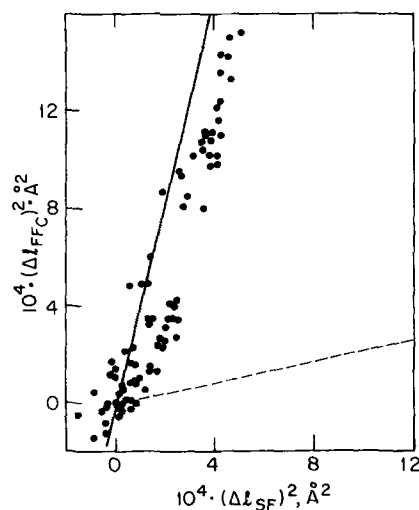


FIG. 4. The change in mean-square amplitude of vibration of the  $\text{FF}_{\text{cis}}$  atom pairs corresponding to a change in mean-square amplitude of the SF bond in  $\text{SF}_6$ . Dashed line calculated for pure  $\nu_3$  excitation. Solid line calculated for thermal equilibrium among vibrational modes. Points represent experimental observations for various degrees of pumping of the  $\nu_3$  mode under collisional conditions.

dinarily the liquid nitrogen cold trap condensed almost all of the SF<sub>6</sub> emerging from the nozzle. If the molecules were irradiated with a frequency near the absorption maximum, however, the reading of the ionization gauge downstream of the cold trap was more than 10% higher than when the laser was tuned to a nonresonant frequency or turned off. Apparently vibrationally excited molecules have a reduced probability of condensing on a cold surface.

When molecular parameters plotted in Figs. 1–4 were determined, it was assumed that each internuclear probability distribution possessed a Gaussian shape characteristic of an ensemble in equilibrium at a given temperature. Although it was not assumed that each peak corresponded to the same temperature, results showed that the effective temperatures of the SF, FF<sub>cis</sub>, and FF<sub>trans</sub> seldom differed among themselves by more than the uncertainties in the temperatures. In particular, Fig. 4 shows that the vibrational energy distribution among the modes is that of a Boltzmann distribution rather than of molecules excited only in the  $\nu_3$  mode.<sup>20</sup> In principle, the diffraction intensities contain more detailed information about vibrations than just the mean-square amplitudes. If a sample were to consist of several populations each characterized by a different temperature or different state of excitation, the peaks in the radial distribution function would no longer be simple Gaussian functions. In the present study with a fairly restricted scattering angle and, hence, a somewhat limited resolving power, only a rather coarse test of sample homogeneity could be made. It proceeded as follows.

In keeping with the fact that some molecules in the gas jet pass directly through the most intense region of the laser focus while others traverse only the periphery, a model comprised of two different populations was adopted. It was assumed that one of the populations was at some elevated temperature with mole fraction  $X_T$  while the other remained at room temperature. Least squares refinements were then carried out upon the diffraction intensities as a function of  $X_T$  and the molecular parameters of the hotter population. Molecules at room temperature were assigned distances and amplitudes corresponding to values found from the control plates. Equally good fits of intensities were found in the range  $1.0 > X_T > 0.5$ . As  $X_T$  dropped below 0.5 (with the hot population becoming progressively hotter to preserve the mean-square amplitudes) the fit worsened. Similar behavior was observed in refinements of thermally heated SF<sub>6</sub>. To achieve a greater discrimination between uniform and nonuniform populations a greater resolving power (higher scattering angle range) is needed.

## B. Uncertainties

Although it is customary in reporting results of electron diffraction investigations to tabulate molecular parameters and their estimated uncertainties,<sup>21</sup> the large body of data in the present paper precludes adherence to such a practice, here. Nevertheless, it is worthwhile in this unconventional application to provide a convenient compilation of uncertainties in derived molecular quantities. This is done in Fig. 5 which displays uncertainties

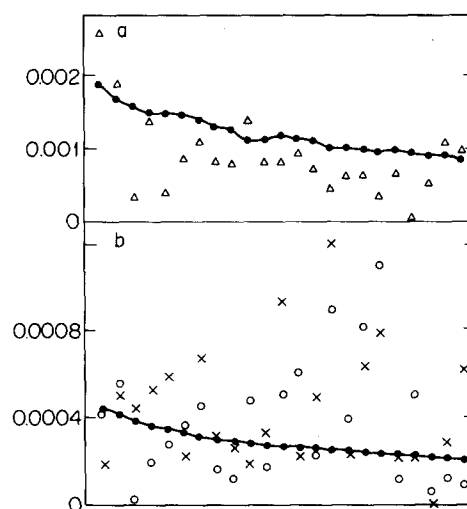


FIG. 5. Graphical representation of two measures of uncertainties in amplitudes of vibration (in Å) corresponding to standard deviations from *individual* diffraction plate refinements. Each run of three or four plates is represented once and plotted, arbitrarily, in order of decreasing  $\sigma_{LS}$  for FF<sub>cis</sub>. Solid points are  $\sigma_{LS}$  values derived from the least-squares error matrix (see the text) for SF and FF<sub>cis</sub> (lower curve, where errors are almost the same for both amplitudes) and for FF<sub>trans</sub> (upper curve). Other symbols portray plate to plate reproducibility  $\sigma_{rep}$  of Eq. (1), text; SF (crosses), FF<sub>cis</sub> (open circles), and FF<sub>trans</sub> (triangles).

in the amplitudes of vibration plotted in Figs. 1 and 2, arbitrarily arranging results in order of decreasing standard deviations  $\sigma_{LS}(l_{SF})$  derived by least squares. Each set of three or four plates taken under a given condition (of pressure, power, and frequency) is represented by the (single plate)  $\sigma_{LS}$  for the amplitudes  $l_{SF}$ ,  $l_{FF(cis)}$ , and  $l_{FF(trans)}$ , and also by the reproducibility index  $\sigma_{rep}$ . Standard deviations in the SF bond length were about half those in the SF and FF(*cis*) amplitudes. It is noteworthy that, if three or four sets possessing anomalously poor reproducibility are excluded, the means of the  $\sigma_{rep}$  values are very close to the  $\sigma_{LS}$  values. Although such a correspondence would be quite unremarkable in a series of measurements characterized by random errors, it is well known that diffraction analyses suffer from poorly understood systematic errors as discussed in paper I. Apparently the treatment of data we proposed in the foregoing successfully bypasses many of the systematic troubles and gets down virtually to the random noise.

One source of error not revealed by  $\sigma_{LS}$  and only occasionally manifested in  $\sigma_{rep}$  is the unintentional heating of the nozzle by fringe radiation from the focused laser spot. This complication, encountered in troublesome form primarily when delays occurred between opening the laser shutter and beginning the diffraction exposures, does not, of course, spoil the derivation of precise amplitudes. It simply makes uncertain how much of the increase is due to direct pumping. As outlined in paper I, Sec. IIB, a comparison between the exposures of patterns of pumped molecules and their controls affords a measure of the thermal versus the optical excitation. Results for our pumped samples are compared with

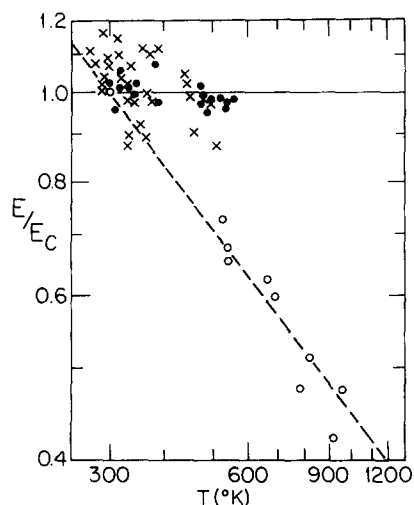


FIG. 6. Relative scattered electron intensities ( $E/E_{\text{control}}$ ) as a function of vibrational temperature  $T$  inferred from  $FF_{cis}$  amplitudes of vibration. Crosses and closed circles represent optical excitation experiments at 300 and 600 Torr stagnation pressures, respectively, and do not reveal systematic intensity losses associated with translational excitation. Open circles represent thermal excitation via heated nozzle tip (stagnation pressure  $\approx 300$  Torr). Intensity losses associated with increasing translational heating are evident.

those from a laser-heated nozzle in Fig. 6. The scatter in exposures of pumped plates suggests that all of the 600 Torr runs and most of the 300 Torr runs were disturbed less than  $25^\circ$  by direct heating. A few of them may have experienced temperature rises of twice this. By comparison, standard deviations in amplitudes of vibration corresponded to uncertainties in temperature of  $30^\circ$ – $35^\circ$  (SF),  $15^\circ$ – $20^\circ$  ( $FF_{cis}$ ), and  $100^\circ$  ( $FF_{trans}$ ). Evidently, then, except for the marginal *trans* parameter, the largest uncertainty in the present work is the direct heating. Now that this source of error is recognized it can be avoided by a better experimental design.

#### IV. DISCUSSION: PRELIMINARY COMMENTS

It is evident that electron diffraction is sufficiently sensitive to detect and follow the absorption of infrared radiation by molecules in a gas jet under appropriate conditions. The most useful and direct information derived is, of course, the set of interatomic amplitudes of vibration corresponding to the various pairs of internuclear distances (Figs. 1, 2, and 4). It is remarkable to observe, however, that the absorption of energy can even be detected in the molecular size (Fig. 3) which expands slightly when a photon is ingested.

Absorption bands as measured by electron diffraction tend to be distorted from those measured by direct absorption of weak infrared beams.<sup>19</sup> The feet of the bands seen by diffraction (and seen most accurately in the band of highest quality  $FF_{cis}$ ) correspond to those of the 300 K spectrum. When molecules are irradiated off resonance, little energy is absorbed and the vibrational temperature is therefore close to 300 K. Near the band centers, excitation is considerable, the mean temperature at which photons are absorbed is closer to 400 K, and the peak is

red shifted in the same manner as the spectroscopic curve at 400 K.

A direct comparison between the present results obtained by pumping a flowing jet with a modest cw laser and the numerous results for static gas systems, obtained over a wide range of fluences and pressures, is not a simple matter. In order to recognize the correspondence it is essential to understand the special aspects of gas dynamics and collisional assistance in absorption cross sections that differentiate processes in supersonic jets from those in static systems. A beginning in this direction can be made by reviewing results to date reported for microjets. Two other studies of gas jets pumped by focused cw lasers have appeared. One, by Arvedson and Kohl,<sup>6,7</sup> also measured vibrational excitation by electron diffraction. Gas pressures were, for the most part, much lower than ours and observed increases in amplitudes of vibration, about  $0.001 \text{ \AA}$ , were small. The other, a particularly informative study by Coulter, Grabiner, Casson, Flynn, and Bernstein,<sup>5</sup> measured absorption with the aid of a bolometric detector and found up to 0.22 quanta absorbed at much lower power densities than applied by Arvedson and Kohl, and ourselves. A continuation of the Coulter *et al.* work by Lester, Coulter, Casson, Flynn, and Bernstein<sup>22</sup> revealed a considerable enhancement of excitation when pumping took place within a transparent nozzle.

It had been our original supposition that the principal excitation would occur when molecules streamed through the most intense region of the focused laser beam. Observations to date, however, suggest that this is frequently not the case. In our experiment, with the power density at the center of the focused spot typically  $15$ – $25 \text{ KW/cm}^2$  (cf. about  $300 \text{ W/cm}^2$  for Coulter *et al.*), it was necessary to withdraw the spot center to a position about  $0.3$ – $0.35 \text{ mm}$  away from the nozzle tip to avoid heating and damaging the nozzle. This still left a fringe power density of  $2$ – $4 \text{ KW/cm}^2$  at the nozzle tip, an intensity quite large enough to pump molecules in the region of high collisional rate immediately outside the nozzle. As reported in several papers,<sup>23</sup> only a fraction of a percent of  $\text{SF}_6$  molecules at any instant are in rotational states capable of being pumped by a single  $\text{CO}_2$  line at the modest powers employed in the present work. (At higher intensities, power broadening alters the situation.) In order to achieve absorption by a substantial fraction of the molecules in a jet, rotational relaxation by collision is essential. In our experiments, excitations of up to 2 photons/molecule were observed when collision rates were sufficiently high.

Molecules flowing through our laser beam experienced irradiation for the order of  $1 \mu\text{s}$ . Because we can calculate the mean fluence  $\bar{\Phi}$  according to Eq. (12) of paper I and measure the mean photon uptake  $\langle n \rangle$ , as well, it is simple to compute the average interaction cross section

$$\bar{\sigma} = \langle n \rangle / \bar{\Phi} h\nu . \quad (2)$$

Although this is straightforward, it is nearly meaningless because of the rapid variation of  $\sigma$  along the gas jet associated with the rapidly varying collision frequency.

Such a variation was revealed most directly by the experiments of Coulter *et al.*<sup>5</sup> who found that the excitation of supersonic microjets takes place within a very short distance from the nozzle tip. A rough, semiquantitative treatment of the collisionally assisted excitation process has appeared elsewhere.<sup>8</sup> It is able to account, approximately, for results obtained under the very different experimental conditions of Coulter *et al.*, and of ourselves, and will be expanded upon in paper III.<sup>24</sup> The fact that the data of Arvedson and Kohl<sup>7,25</sup> lie close to our continuous curve relating absorption to throughput suggests that their results may also have involved collisional assistance. Their experimental conditions are not reported completely enough, however, to make it possible to apply the proposed treatment to their results.

The picture which has emerged suggests that the absorption cross sections appropriate for molecules at various positions along supersonic jets are comparable to those in static systems irradiated with a similar ratio of photon-molecule to molecule-molecule collision rates.<sup>8</sup> In the jets, however, the precipitous drop in molecular collision rate limits the strong absorption to a very small region beyond the nozzle tip. It also introduces a great disparity between translation-rotation temperature and vibrational temperature because the collision number for rotational relaxation is orders of magnitude lower than that for  $V-T$  relaxation.<sup>26</sup> In a microjet of appropriate dimensions it is simple to control the number of collisions experienced by the molecules before they attain their terminal temperature drop to be intermediate between the number required for  $V-T$  and for  $V-V$  and  $T-R$  relaxation. In typical runs our microjets drop over 100° in translational temperature after leaving the nozzle while traveling the distance of a nozzle diameter and experiencing from a few dozen to a few hundred collisions (controlled by the sample pressure). They have dropped 200° by the time they are probed by the electron beam, and ultimately fall to about 20 K or less if nozzle exit pressures exceed 100 Torr.<sup>24</sup> The several hundred degrees of vibrational excitation achieved by pumping remains frozen in internal motions, available for subsequent interactions if desired. This possibility may make pumped jets useful reagents in molecular beam studies of chemical kinetics.

#### ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under grant number CHE-7926480. We gratefully acknowledge a generous allowance of computing time from the University of Michigan Computing Center.

- <sup>1</sup>See, for example, N. Bloembergen and E. Yablonoitch, *Phys. Today* 31 (No. 5), 23 (1978); R. V. Ambartzumian and V. S. Letokhov, *Acc. Chem. Res.* 10, 61 (1977).
- <sup>2</sup>J. D. McDonald, *Annu. Rev. Phys. Chem.* 30, 29 (1974); P. A. Schulz, Aa. S. Sudbe, D. J. Krajnovich, H. S. Kwok, Y. R. Sen, and Y. T. Lee, *ibid.* 30, 379 (1979); M. Kneba and J. Wolfram, *ibid.* 31, 47 (1980).
- <sup>3</sup>J. I. Steinfeld, I. Burak, D. G. Sutton, and A. V. Nowak, *J. Chem. Phys.* 52, 5421 (1970); D. S. Frankel, *ibid.* 65, 1696 (1976); T. F. Deutsch, *Opt. Lett.* 1, 25 (1977); D. Ham and M. Rothchild, *ibid.* 1, 28 (1977).
- <sup>4</sup>E. Grunwald, K. J. Olszyna, D. F. Dever, and P. M. Keehn, *Megawatt Infrared Laser Chemistry* (Wiley, New York, 1978).
- <sup>5</sup>D. R. Coulter, F. R. Grabiner, L. M. Casson, G. W. Flynn, and R. B. Bernstein, *J. Chem. Phys.* 73, 281 (1980).
- <sup>6</sup>M. M. Arvedson and D. A. Kohl, *Chem. Phys. Lett.* 64, 119 (1979).
- <sup>7</sup>M. M. Arvedson and D. A. Kohl, *J. Chem. Phys.* (in press).
- <sup>8</sup>L. S. Bartell, S. R. Goates, and M. A. Kacner, *Chem. Phys. Lett.* 76, 245 (1980).
- <sup>9</sup>See, for example, L. S. Bartell, in *Physical Methods in Chemistry*, edited by A. Weissberger and B. W. Rossiter (Interscience, New York, 1973), 4th edition.
- <sup>10</sup>L. S. Bartell, M. A. Kacner, and S. R. Goates, *J. Chem. Phys.* 75, 2730 (1981).
- <sup>11</sup>L. S. Bartell, D. A. Kohl, B. L. Carroll, and R. M. Gavin, Jr., *J. Chem. Phys.* 42, 3079 (1965).
- <sup>12</sup>H. L. Sellers, L. Schäfer, and R. A. Bonham, *J. Mol. Struct.* 49, 125 (1978).
- <sup>13</sup>C. Tavard, D. Nicholas, and M. Rouault, *J. Chim. Phys. Phys.-Chim. Biol.* 64, 540 (1967).
- <sup>14</sup>L. S. Bartell, *J. Mol. Struct.* 63, 259 (1980).
- <sup>15</sup>M. Fink and M. Kelley, "Austin Symposium on Molecular Structure, Austin, Texas, March 3, 1980," *J. Chem. Phys.* (submitted).
- <sup>16</sup>S. R. Goates and L. S. Bartell (unpublished).
- <sup>17</sup>JANAF Thermochemical Tables, *Natl. Stand. Ref. Data Ser.*, *Natl. Bur. Stand.* 37 (1965).
- <sup>18</sup>R. S. McDowell, J. P. Aldridge, and R. F. Holland, *J. Phys. Chem.* 80, 1203 (1976).
- <sup>19</sup>A. V. Nowak and J. L. Lyman, *J. Quant. Spectrosc. Radiat. Transfer* 15, 945 (1975).
- <sup>20</sup>For the method of relating nonequilibrium vibrational distributions to radial distribution functions and electron diffraction, see M. A. Kacner and L. S. Bartell, *J. Chem. Phys.* 71, 192 (1979).
- <sup>21</sup>L. S. Bartell, K. Kuchitsu, and H. M. Seip, *Acta Crystallogr. Sect. A* 32, 1013 (1976).
- <sup>22</sup>M. I. Lester, D. R. Coulter, L. M. Casson, G. W. Flynn, and R. B. Bernstein, *J. Phys. Chem.* 85, 751 (1981).
- <sup>23</sup>See, for example, I. Burak, J. I. Steinfeld, and D. G. Sutton, *J. Quant. Spectrosc. Radiat. Transfer* 9, 959 (1969).
- <sup>24</sup>L. S. Bartell, M. A. Kacner, and S. R. Goates (in progress).
- <sup>25</sup>D. A. Kohl (unpublished research).
- <sup>26</sup>T. L. Cottrell and J. C. McCoubrey, *Molecular Energy Transfer in Gases* (Butterworths, London, 1961); C. O'Neal and R. S. Brokaw, *Phys. Fluids* 6, 1675 (1963).