

## Resonant electronic to vibrational energy transfer from Na to CH<sub>4</sub> and CD<sub>4</sub>

T. F. Gallagher, G. A. Ruff,\* and K. A. Safinya

*Molecular Physics Laboratory, SRI International, Menlo Park, California 94025*

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We have observed sharply resonant collisional energy transfer from electronic excitation of the Na  $ns$  ( $n = 5-11$ ) states to vibrational excitation in CH<sub>4</sub> and CD<sub>4</sub> leading to resonant cross sections of  $\sim 300 \text{ \AA}^2$ . However, not all energetically resonant transfers occur with large cross sections. The apparent selection rules for the process and the magnitude of the cross sections suggest that the process be described in terms of low-energy electron-molecule scattering.

### INTRODUCTION

In collisional excitation or deexcitation of atoms it is expected that if the change in electronic energy  $\Delta E$  matches the energy of an internal motion of the collision partner, such as vibration in a molecule, the cross section will be dramatically increased. Thus if one could tune  $\Delta E$  across the molecular vibrational transition energy of a molecule it should be possible to observe a large increase in the cross section at resonance. Although this has been done in a crude way by changing molecular-collision partners<sup>1</sup> it is the regular Rydberg series of an atom which presents the best opportunity for a systematic study. Here we report such a study of the collisional deexcitation of Na  $ns$  ( $n = 5-11$ ) states by CH<sub>4</sub> and CD<sub>4</sub>. As  $n$  is changed the available values of  $\Delta E$  change, and when a resonance with an ir-active  $\nu_3$  or  $\nu_4$  vibrational energy occurs, we observe a dramatic increase in the cross section. Independently we have shown the increases to be due to the resonant transition in the atom. Since the vibrational frequencies of CH<sub>4</sub> and CD<sub>4</sub> are different, the resonances occur for different  $n$  and are hence isotope specific. The importance of the energy resonance in electronic-to-rotational energy transfer has already been shown by Smith *et al.*,<sup>2</sup> who did the inverse experiment, observing the selective population of resonant final atomic electronic states after the collision. Equally as interesting as the necessity of energy resonance is that it is not sufficient to produce an enhanced cross section. In many energetically resonant cases we do not observe any enhancement of the cross section, indicating the existence of additional approximate selection rules for the process. The knowledge of the selection rules is, of course, most helpful in gaining insight into the physical process involved. In fact it appears that describing the collision of the excited Na-CH<sub>4</sub> in terms of electron-CH<sub>4</sub> scattering is the most consistent with our observations. In addition to the intrinsic interest

of the collision process we might note that it is an efficient method for transferring energy from an atom to a specific molecular vibration which may form the basis of an energy-transfer molecular laser.

### EXPERIMENTAL APPROACH

The method we use is laser-induced fluorescence of Na atoms in a cell to which CH<sub>4</sub> or CD<sub>4</sub> gas has been added. The general approach can be understood with the aid of Fig. 1 which illustrates the study of the Na 6s state. Two dye-laser pulses excite the Na atoms in two steps,  $3s \rightarrow 3p$  and  $3p \rightarrow 6s$ , and we observe the time and wavelength-resolved fluorescence both from the initially excited 6s state and the 5p state, which is populated by the collisional e-v (electronic-to-vibrational) transfer. Measurements of the decay rates and fluorescence yields for these states as functions of CH<sub>4</sub> and CD<sub>4</sub> pressures yield the total depopulation cross sections and the state-specific e-v transfer cross sections.

The apparatus is described in detail elsewhere,<sup>3</sup> so we shall only outline its major features. The pyrex vapor cell is a cylinder 10 cm long and 2.5 cm in diameter. It is heated to 430 K and up to 2 torr of CH<sub>4</sub> or CD<sub>4</sub> is added. The overlapping laser beams pass through the cell along its axis, and we observe the fluorescence at 90° through the side wall of the cell using a photomultiplier and a monochromator or filter. The photomultiplier signals are averaged using a boxcar averager and are analyzed with a laboratory computer.

The resonant nature of the electronic-to-vibrational transfer is clearly illustrated in the total depopulation cross sections  $\sigma_{ns}$  of the Na  $ns$  states obtained by measuring the decay rates of the  $ns$  states versus CH<sub>4</sub> or CD<sub>4</sub> pressure. For example, in Fig. 2 we show the decay rate  $K_{6s}$  of the Na 6s state versus CH<sub>4</sub> and CD<sub>4</sub> pressure. The decay rate  $K_{6s}$  is related to the collision cross section by

$$K_{6s} = 1/\tau_{6s} + N\sigma_{6s}\bar{v}, \quad (1)$$

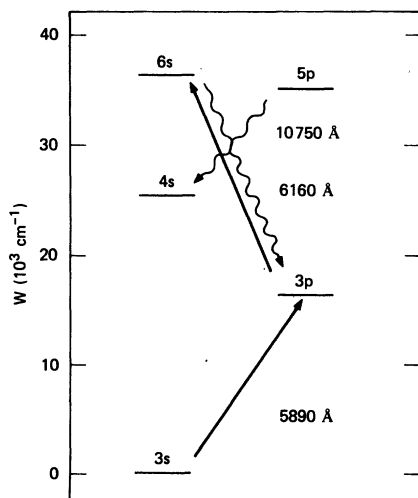


FIG. 1. Relevant energy levels for the study of the Na  $6s$  and  $5p$  states. The straight upward arrows indicate the laser pumping steps, the heavy arrow indicates the collisional transfer, and the wavy arrows indicate the observed fluorescence.

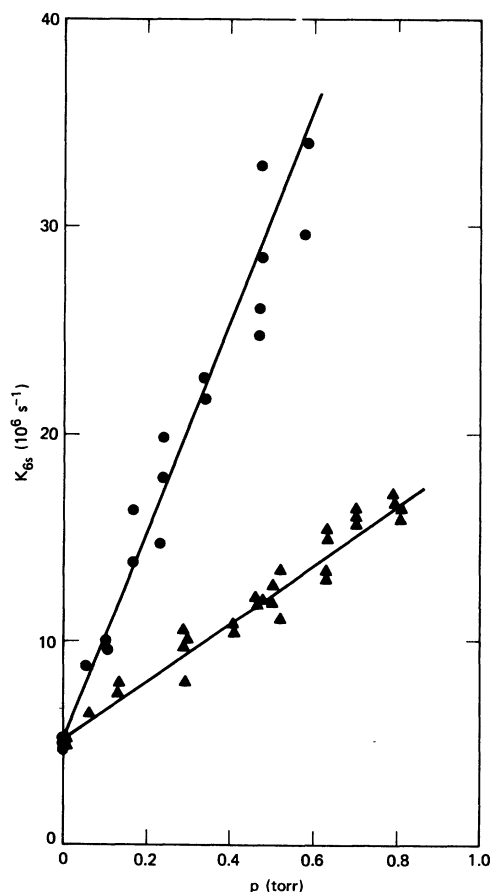


FIG. 2. Decay rate of the Na  $6s$  state versus CH<sub>4</sub> (●) and CD<sub>4</sub> (▲) pressure.

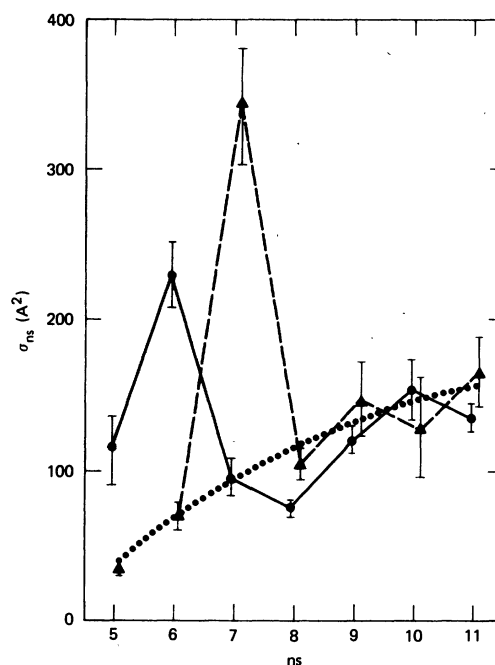


FIG. 3. Total depopulation cross sections  $\sigma_{ns}$  for the Na  $ns$  states with CH<sub>4</sub> (●, —) and CD<sub>4</sub> (▲, ---). The smooth dotted curve (....) shows the expected depopulation cross section in the absence of resonant e-v transfer.

where  $\tau_{6s}$  is the radiative lifetime of the Na  $6s$  state,  $N$  is the number density of the CH<sub>4</sub> or CD<sub>4</sub>, and  $\bar{v}$  is the average collision velocity. We present the data as cross sections to make the relation to atomic size clear, but as shown by Fig. 2 we measure rate constants. For CH<sub>4</sub> and CD<sub>4</sub> a cross section of  $1 \text{ \AA}^2$  corresponds to a rate constant of  $0.222 \times 10^6$  and  $0.209 \times 10^6 \text{ s}^{-1} \text{ torr}^{-1}$ , respectively. As shown by Fig. 3 and tabulated in Table I, the dependence of  $\sigma_{ns}$  on  $n$  is a smooth curve, similar to that obtained for N<sub>2</sub> (Ref. 4) except that the  $\sigma_{5s}$  and  $\sigma_{6s}$  points are far above the curve for CH<sub>4</sub>, as is  $\sigma_{7s}$  for CD<sub>4</sub>. The enhanced cross sections appear in different states for CH<sub>4</sub> and CD<sub>4</sub> due to the different molecular-vibrational frequencies (it is important to note that the *only* differences between CH<sub>4</sub> and CD<sub>4</sub> are in the H and D masses which change the vibrational and rotational frequencies). In Table II, we list the frequencies of the atomic transitions from the  $5s$ ,  $6s$ , and  $7s$  states and the resonant molecular bands to which we attribute the resonant e-v transfer.<sup>5-7</sup>

Although the dramatic increases in the total depopulation cross sections and the resonances of Table II are suggestive, a critical test is to observe the atomic population's being transferred

TABLE I. Total depopulation cross sections for  $\sigma_{ns}$  Na states.

Na state	$\sigma_{ns}(\text{CH}_4)$ ( $\text{\AA}^2$ )	$\sigma_{ns}(\text{CD}_4)$ ( $\text{\AA}^2$ )
5s	113(23)	35(5)
6s	230(22)	71(10)
7s	96(13)	344(39)
8s	76(5)	105(11)
9s	121(9)	148(25)
10s	155(20)	129(34)
11s	136(10)	167(24)
4p	72(10)	71(10)
5p	51(7)	49(7)
5d		43(14)

to the final states indicated in Table II. As examples, let us consider the 6s and 7s states which, according to Table II, can be resonantly depopulated by  $\text{CH}_4$  and  $\text{CD}_4$ , respectively.

To observe the Na population's being transferred from the initially populated 6s state to the 5p state, we observed the  $5p \rightarrow 4s$  fluorescence at 10 750  $\text{\AA}$  as a function of the  $\text{CH}_4$  and  $\text{CD}_4$  pressure. The pressure dependence of the decay rate of the 5p state yields immediately  $\sigma_{5p}(\text{CH}_4) = 51(7) \text{\AA}^2$  and  $\sigma_{5p}(\text{CD}_4) = 49(7) \text{\AA}^2$ . From the total (time integrated) fluorescence yields  $Y_{3p-6s}$  and  $Y_{4s-5p}$ , of the  $6s \rightarrow 3p$  transition at 5150  $\text{\AA}$  and the  $5p \rightarrow 4s$  transition at 10 750  $\text{\AA}$  as functions of  $\text{CH}_4$  and  $\text{CD}_4$  pressure, we can determine the state-specific cross sections  $\sigma_{5p-6s}$ . Following the development of Ref. 3 we can express the ratio  $Y_{4s-5p}/Y_{3p-6s}$  as

$$Y_{4s-5p}/Y_{3p-6s} = K_{5p-6s} A_{4s-5p}/K_{5p} A_{5p-6s}, \quad (2)$$

where  $A_{n'l'-nl}$  is the Einstein A coefficient for the transition  $nl \rightarrow n'l'$  and  $K_{5p-6s}$  is the rate at which Na atoms in the 6s state decay to the 5p state (explicitly  $K_{5p-6s} = A_{5p-6s} + N\sigma_{5p-6s}\bar{v}$ ). From Eq. (2) it is apparent that the observed yields at 5150 and 10 750  $\text{\AA}$  may be normalized at zero  $\text{CH}_4$  or  $\text{CD}_4$  pressure using the known Na A coefficients and radiative lifetimes.<sup>8</sup> In Fig. 4 we show the

ratio  $Y_{4s-5p}/Y_{3p-6s}$  vs  $\text{CH}_4$  and  $\text{CD}_4$  pressure, which shows qualitatively that  $\sigma_{5p-6s}(\text{CH}_4) \gg \sigma_{5p-6s}(\text{CD}_4)$ . In Fig. 4 we also show the best fit of the data to Eq. (2) using the measured decay rates of the 5p state and the known atomic A coefficients.<sup>8</sup> The fit yields the values of  $\sigma_{5p-6s}$  given in Table II, where we have given for reference the geometric cross section  $\sigma_{\text{geom}}$ , for the final state of each of the transitions considered in Table II. Note that  $\sigma_{5p-6s}(\text{CD}_4)$  is almost exactly equal to the amount by which  $\sigma_{6s}(\text{CH}_4)$  lies above the smooth  $\sigma_{ns}$  curve.

To check that the large cross section for depopulation of the 7s state by  $\text{CD}_4$  was in fact due to the resonant  $7s \rightarrow 5d$  transfer, we observed the population in the 5d state as a function of  $\text{CH}_4$  and  $\text{CD}_4$  pressure when the 7s state was populated by the laser. This was done by observing the  $5d \rightarrow 3p$  fluorescence at 4980  $\text{\AA}$ . The time dependence of the  $5d \rightarrow 3p$  fluorescence indicates that the population is transferred directly from the 7s state to the 5d state, not via the long lived (700 ns) 6p state. The rise and fall times of the  $5d \rightarrow 3p$  fluorescence correspond to the 5d and 7s decay rates, respectively. These rates are fast,  $10 \times 10^6$  and  $7 \times 10^6 \text{ s}^{-1}$  at 0.06-torr  $\text{CH}_4$ , making it relatively easy to see that the population is not transferred via the 6p state. In that case the  $5d \rightarrow 3p$  fluorescence would reflect, especially at low (0.06 torr) pressures, the slow decay rate  $2 \times 10^6 \text{ s}^{-1}$ , of the 6p state; however, it does not. Thus we assume that only a negligible amount of population is transferred to the 5d state via the 6p state and that the population is transferred directly from the 7s to the 5p state. Following Ref. 3 we can then express the ratio of fluorescence yields  $Y_{3p-5d}/Y_{3p-7s}$  (at 4980 and 4750  $\text{\AA}$ ) as

$$Y_{3p-5d}/Y_{3p-7s} = K_{5d-7s} A_{3p-5d}/A_{3p-7s} K_{5d}. \quad (3)$$

Note that, at zero pressure of  $\text{CH}_4$  or  $\text{CD}_4$ ,  $K_{5d-7s} = 0$ . Thus we must calibrate the relative response of our detection system at 4980 and 4750  $\text{\AA}$ , which we did using a 2050  $^\circ\text{C}$  black-body source. In Fig. 5 we show the ratio  $Y_{3p-5d}/Y_{3p-7s}$  vs  $\text{CH}_4$  and  $\text{CD}_4$  pressure. By fitting Eq. (3) to these data, as shown in Fig. 5, we can extract the state-spec-

TABLE II. Na and  $\text{CH}_4$ ,  $\text{CD}_4$  frequencies.

Na transition	Na frequency ( $\text{cm}^{-1}$ )	Isotope	Mode	CH <sub>4</sub> , CD <sub>4</sub> transitions		
				Branch	Branch center frequency ( $\text{cm}^{-1}$ )	Branch width ( $\text{cm}^{-1}$ )
4p → 5s	2930	CH <sub>4</sub>	$\nu_3$	P	2940	60
5p → 6s	1331	CH <sub>4</sub>	$\nu_4$	R	1340	60
5d → 7s	975	CD <sub>4</sub>	$\nu_4$	P	965	50

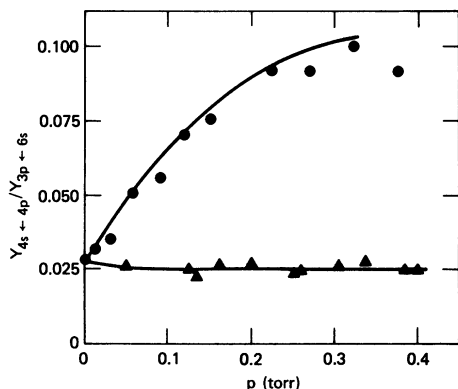


FIG. 4. Ratio of the  $5p \rightarrow 4s$  to  $6s \rightarrow 3p$  fluorescent yields versus  $\text{CH}_4$  (●) and  $\text{CD}_4$  (▲) pressure. The fit to Eq. (2) is shown by the solid lines.

ific cross sections  $\sigma_{5d-7s}$  of Table III. Again we find that  $\sigma_{5d-7s}(\text{CD}_4)$  is roughly equal to the amount by which  $\sigma_{7s}(\text{CD}_4)$  lies above the smooth curve. We only made a rough check that  $\sigma_{5d}(\text{CH}_4)$  was equal to  $\sigma_{5d}(\text{CD}_4)$  to within a factor of two because the effect on the  $5d$  decay rate is only 12% at the highest pressure used.

We carried out an analogous experiment for the  $5s$  state to show that the  $5s \rightarrow 4p$  transfer is responsible for the large value of  $\sigma_{5s}(\text{CH}_4)$ . This experiment yielded the values for  $\sigma_{4p}$  given in Table I, as well as the state-specific cross sections  $\sigma_{4p-5s}$  listed in Table III. Again we find that  $\sigma_{4p-5s}(\text{CH}_4)$  is roughly equal to the amount by which  $\sigma_{5s}(\text{CH}_4)$  lies above the smooth curve. As a systematic check, we also observed the fluorescence emanating from lower-lying states when we populated the  $8s$  state for which the total depopulation cross sections are the same for  $\text{CH}_4$  and  $\text{CD}_4$ ; however, the yields with  $\text{CH}_4$  and  $\text{CD}_4$  differed by less than 10%, indicating no isotopic effect.

#### DISCUSSION

As we mentioned earlier, the resonances or near resonances which do not lead to enhanced cross sections yield additional valuable information which we can cast in the form of selection rules for  $\Delta E$ ,  $\Delta v$ ,  $\Delta l$ , and  $\Delta n$ .

We can infer the width of the resonance from the near-resonant cases which satisfy all the apparent selection rules. The data of Fig. 1 imply a width of  $<100 \text{ cm}^{-1}$ . However, a more stringent limit is implied by the  $\text{Na } 4p$  state for which  $\sigma_{4p}(\text{CH}_4) = \sigma_{4p}(\text{CD}_4)$  in spite of the fact that the  $1098 \text{ cm}^{-1} 4p \rightarrow 3d$  transition is only  $50 \text{ cm}^{-1}$  from the center of the  $\text{CD}_4 \nu_4 R$  branch. This is close to the minimum width  $16 \text{ cm}^{-1}$ , implied by the uncertainty principle for a thermal collision with a cross section of  $300 \text{ Å}^2$ . Thus we can conclude that the

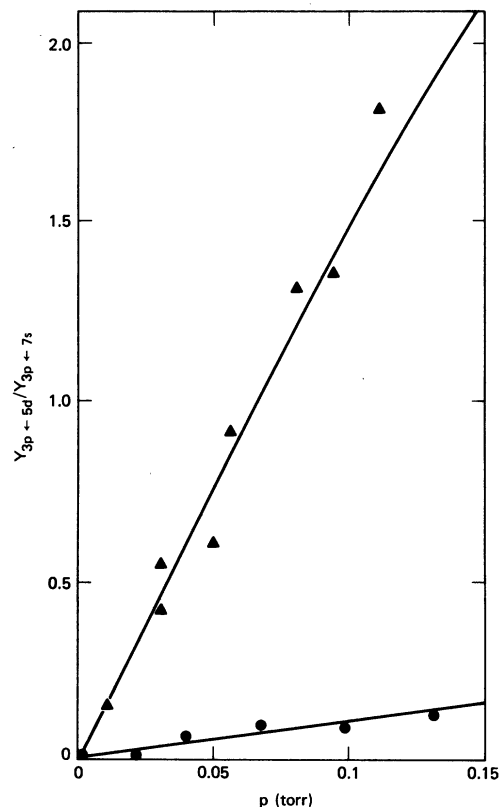


FIG. 5. Ratio of the  $5d \rightarrow 3p$  to  $7s \rightarrow 3p$  fluorescent yields versus  $\text{CH}_4$  (●) and  $\text{CD}_4$  (▲) pressure. The fit to Eq. (3) is shown by the solid lines.

width lies between 16 and  $50 \text{ cm}^{-1}$ .

Similarly, we note that while the  $5s \rightarrow 4p$  transition is resonant with the  $\text{CD}_4 \nu_1 + \nu_4$  combination band,  $\sigma_{4p-5s}(\text{CD}_4) \sim 0$ . Thus combination bands, and probably overtones, are not likely to lead to resonant effects. This is not surprising since the optical absorption of the combination band is roughly 10% of the absorption of the  $\nu_3$  band,<sup>7</sup> and previous measurements show that the transfer of an additional vibrational quantum reduces the cross section by about a factor of ten.<sup>1</sup>

If we restrict our attention to cases in which the atomic transition frequency lies in the observed molecular bands of the  $\text{CH}_4$  and  $\text{CD}_4$  ir-active  $\nu_3$  and  $\nu_4$  modes which lead to the observed reso-

TABLE III. State-specific cross sections  $\sigma_{n'l' \leftarrow nl}$ .

Transition	$\sigma_{n'l' \leftarrow nl}$		$\sigma_{\text{geom}}$ ( $\text{Å}^2$ )
	$\text{CH}_4$ ( $\text{Å}^2$ )	$\text{CD}_4$ ( $\text{Å}^2$ )	
$\sigma_{4p \leftarrow 5s}$	103(22)	10(14)	86
$\sigma_{5p \leftarrow 6s}$	135(22)	9(4)	260
$\sigma_{5d \leftarrow 7s}$	12(4)	215(33)	550

TABLE IV. Na-CH<sub>4</sub>, CD<sub>4</sub> resonances which do not lead to resonant e-v transfer.

Na transition		Molecular transition		
States	Frequency (cm <sup>-1</sup> )	Isotope	Mode	Branch
8s → 7s	956	CD <sub>4</sub>	ν <sub>4</sub>	P
9s → 7p	1033	CD <sub>4</sub>	ν <sub>4</sub>	R
10s → 8s	1015	CD <sub>4</sub>	ν <sub>4</sub>	R
11s → 8p	974	CD <sub>4</sub>	ν <sub>4</sub>	P, Q
10s → 6d	2277	CD <sub>4</sub>	ν <sub>3</sub>	R
11s → 7s	2261	CD <sub>4</sub>	ν <sub>3</sub>	Q
11s → 6p	2976	CH <sub>4</sub>	ν <sub>3</sub>	P
10s → 5d	2947	CH <sub>4</sub>	ν <sub>3</sub>	P

nant e-v transfers we find eight resonances which do not lead to resonant e-v transfer, which we list for reference in Table IV. From these cases and the cases of observed resonant enhancement we are able to derive some selection rules for the process. We have observed  $\Delta l = 1$  and 2 cross sections, where  $l$  is the angular momentum of the Na electron. Both have comparable cross sections suggesting that the process does not occur at long range (compared to the radius of the Na atom), for that would favor  $\Delta l = 1$  transitions. This and the large size of the observed cross sections imply that the interaction must take place at about the mean radius of the electrons orbit  $\sim 7^2$  Å. Thus, it is not surprising that the observed cross sections correspond roughly to the geometric cross sections given in Table III.

While we observed  $\Delta l = 1$  and 2 collisions we did not observe a resonant enhancement in the cross section from the  $\Delta l = 0$  8s → 7s transition at 956 cm<sup>-1</sup> in spite of the fact that it is resonant with the CD<sub>4</sub>ν<sub>4</sub> transition. A molecular curve-crossing treatment<sup>9</sup> would not produce such a selection rule, but a simple classical picture does. If the Na atom is in the 8s state the electron's motion is purely radial and if it scatters from a CH<sub>4</sub> or CD<sub>4</sub> molecule at any nonzero radius, only scattering angles of 0 or 180° lead to a final s state, whereas low-energy electron-molecule scattering leading to vibrational excitation is generally isotropic.<sup>10</sup> Thus atomic s-s transitions should not lead to vibrational excitation.

Most of the resonant cases which produce no enhancement require large changes in  $n$  of the Na atom, such as the 974 cm<sup>-1</sup> 11s → 8p transition. In such cases we attribute the lack of enhancement to poor overlap of the radial wave functions and the resulting weak coupling of the atomic states during the collision.

Unfortunately there are no  $\Delta l = 1$  or 2 transitions from the Na  $ns$  states which coincide with isolated Raman modes of CH<sub>4</sub> or CD<sub>4</sub>. The only coincidence occurs between the spherically symmetric ν<sub>1</sub> mode of CH<sub>4</sub> at 2914 cm<sup>-1</sup> and the Na 5s → 4p transition. Unfortunately, the ir-active ν<sub>3</sub> mode also coincides with the Na 5s → 4p transition and for reasons of symmetry we have assumed that it is the ν<sub>3</sub> mode which is excited in the collision.

Since our observations appear to be qualitatively consistent with a description based on electron-molecule scattering, it is interesting to compare the two. Since the process occurs at large orbital radius, roughly the geometric radius of the final Na state, the electron initially has a low kinetic energy ~0.1–0.4 eV and loses nearly all of it to the vibrational motion. This would require that the cross section for vibrational excitation of CH<sub>4</sub> by electron impact have a very high cross section at and slightly above the threshold for vibrational excitation. In fact, the cross section for excitation of the ν<sub>2</sub> and ν<sub>4</sub> modes for CH<sub>4</sub> exhibits just such a cross section.<sup>11</sup> Thus, it appears that the free-electron model qualitatively explains our data, however, quantitative calculations to test the magnitudes of the cross section, the selection rules, and the observed widths, would be most interesting.

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\*Permanent address: Dept. of Physics and Astronomy, Bates College, Lewiston, Maine 04240.

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