NOTE

Spectrum of the High Rotational Levels of CO Populated by Photodissociation of Formaldehyde[1]

Atomic or molecular products of molecular photodissociation are often created with nonthermal energy distributions. In the work described here, we take advantage of such a situation to obtain a clean spectrum of high rotational levels in the CO $A^1\Pi$ ($v = 1$) ← $X^1\Sigma^+$ ($v = 0$) transition. Under thermal conditions, interference from vibrational hot bands, primarily the 2 ← 1 band, can make identification and analysis of this region of the spectrum more difficult.

Upon absorption of a 3.5-eV photon (355 nm), formaldehyde (H_2CO) dissociates into H_2 and CO with an excess energy of about 3.5 eV (1). Most of this energy goes into rotation and translation of the products with little going into vibration of the CO (2, 3). This allows us to probe the rotational structure of the A ← X transition of CO for J'' up to 63.
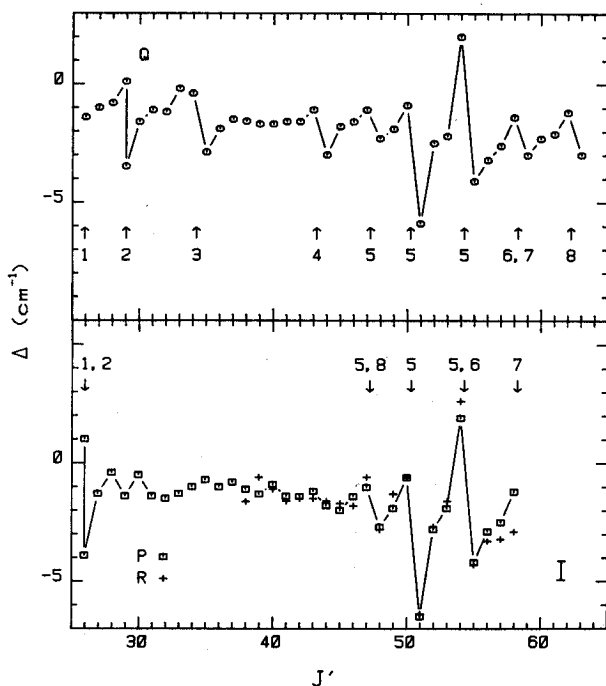

FIG. 1. Calculated line position minus measured line position (in cm^{-1}) for each value of J' for the Q, P, and R branches. The estimated uncertainty of 0.4 cm^{-1} is indicated by the error bar. Arrows indicate perturbations and are labeled with the perturbing state: $1 = {}^1\Delta(1)$, $2 = {}^3\Sigma^+(10)$, $3 = {}^1\Sigma^-(2)$, $4 = {}^3\Sigma^-(3)$, $5 = {}^3\Delta'(6)$, $6 = {}^3\Sigma^+(11)$, $7 = {}^1\Delta(2)$, $8 = {}^1\Sigma^-(3)$, where (n) indicates the vibrational level.

The experimental technique and apparatus have been described previously (*3*). Briefly, the CO spectrum is taken using the technique of vuv laser-excited fluorescence. The formaldehyde is photodissociated by the third harmonic of a Nd:YAG laser (355 nm). The tunable vuv probe light, generated by four-wave mixing in Mg vapor (*4, 5*), excites the product CO to its *A* state and resonances are detected by monitoring fluorescence from this state. A 250-nsec delay between the photolysis and probe lasers allows completion

TABLE I

Line Positions (in cm^{-1}) for Rotational Levels of the CO $A^1\Pi$ ($v = 1$) ← $X^1\Sigma^+$ ($v = 0$) Transition

J''	P	Q	R
23	65967.8	-----	-----
24	948.1	-----	-----
25	927.4	66006.4	-----
26	906.6	65989.5	-----
27	888.7 a	970.5	-----
	883.8	-----	-----
28	863.7	951.0	-----
29	839.7 a	933.7	-----
	-----	930.1	-----
30	816.9	911.1	-----
31	791.5	889.2	-----
32	767.3	867.2	-----
33	741.5	843.4	-----
34	714.7	820.1	-----
35	687.2	798.4	-----
36	658.9	772.5	-----
37	630.6	746.5	65865.0
38	601.0	720.3	840.7
39	571.3	693.3	817.2
40	540.7	665.6	793.0
41	508.9	637.1	767.5
42	477.2	607.9	741.4
43	444.3	577.6	714.6
44	410.6	548.9	687.1
45	377.0	516.4	658.9
46	342.1	484.2	628.7
47	305.9	451.0	601.1
48	269.1	418.8	569.2
49	233.7	384.3	537.3
50	195.1	348.4	511.2
51	155.3	317.8	474.8
52	122.0	278.1	440.3
53	078.3	240.8	402.0
54	036.7	198.8	374.1
55	64991.6	166.5	337.5
56	955.6	126.4	301.0
57	911.5	085.8	263.7
58	867.5	044.0	-----
59	822.0	004.2	-----
60	-----	64961.4	-----
61	-----	918.3	-----
62	-----	873.8	-----
63	-----	831.3	-----

a. The 2 line positions are the split components of the perturbed transition.

NOTE

of the dissociation process. Rotational relaxation for the pressures and J values of interest occurs on a microsecond timescale (3). The high J population is thus not seriously depleted during the 250-nsec delay.

We obtain the spectrum of the $A \leftarrow X$ transition over the range 151.1 to 154.3 nm ($J'' = 23$ to 63) free of interference from other transitions or impurities. The red limit (high J) is set by the presence of the $e^3\Sigma^-$ ($v = 1$) bandhead at 154.28 nm. The blue limit (low J) is set by the thermal population in the low J levels of the background CO. Table I lists our measured line positions and assignments, which complement published line positions (6, 7) covering the range $0 < J'' < 30$. Our vuv frequency calibration is based on the tabulated line positions of Simmons et al. (7) for the bandheads of the $1 \leftarrow 0$ and $0 \leftarrow 0$ bands of $A \leftarrow X$, and is accurate to ~0.25 cm^{-1}. The uncertainty is determining line centers introduced by noise is of the same magnitude.

In the figure, our measured line positions are compared with positions calculated using the equilibrium constants of Goldberg et al. (8) for the X state and of Tilford et al. (6) for the A state. As indicated in the figure, there are several perturbations in this spectral region due to six other states near the A state. All the perturbations can be attributed to known levels, as indicated in the figure. Perturbations at lower J's have previously been observed and analysed (7, 9). A more complete deperturbation analysis of the CO $A^1\Pi$ state, including high J levels, is being done by Field and co-workers (10).

In conclusion, we have demonstrated a spectroscopic advantage gained by studying a photoproduct molecule. Even though the $v'' = 0$, $J'' = 63$ level is about three times higher in energy than the $v'' = 1$, $J'' = 0$ level, it appears much stronger in our spectrum due to the nonthermal distribution of energy among the vibrational and rotational degrees of freedom of the CO photoproduct.

REFERENCES

1. J. H. CLARK, C. B. MOORE, AND N. S. NOGAR, J. Chem. Phys. 68, 1264–1271 (1978).
2. P. HO, D. J. BAMFORD, R. J. BUSS, Y. T. LEE, AND C. B. MOORE, J. Chem. Phys. 76, 3630–3636 (1982).
3. P. HO AND A. V. SMITH, Chem. Phys. Lett. 90, 407–411 (1982).
4. S. C. WALLACE AND G. ZDASIUK, Appl. Phys. Lett. 28, 449–451 (1976).
5. H. JUNGINGER, H. B. PUELL, H. SCHEINGRABER, AND C. R. VIDAL, IEEE J. Quantum Electron. QE16, 1132–1137 (1980).
6. S. G. TILFORD AND J. D. SIMMONS, J. Phys. Chem. Ref. Data 1, 147–187 (1972).
7. J. D. SIMMONS, A. M. BASS, AND S. G. TILFORD, Astrophys. J. 155, 345–358 (1969).
8. L. GOLDBERG AND E. A. MULLER, Astrophys. J. 118, 397–411 (1953).
9. R. W. FIELD, S. G. TILFORD, R. A. HOWARD, AND J. D. SIMMONS, J. Mol. Spectrosc. 44, 347–382 (1972); R. W. FIELD, B. G. WICKE, J. D. SIMMONS, AND S. G. TILFORD, J. Mol. Spectrosc. 44, 383–399 (1972).
10. R. W. FIELD, K. YOSHINO, E. CHIPMAN, C. BROWN, AND A. LEFLOCH, private communication.

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