Nuclear spin relaxation studies of the spin-rotation interaction of ^{13}C in CO in various buffer gases

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Nuclear spin-lattice relaxation times T_1 have been measured for ^{13}C in $^{13}C^{16}O$ in pure CO gas and in CO in Ar, Kr, Xe, N_2, O_2, CO_2, HCl, CH_4, and SF_6 gases as a function of temperature. The relaxation is completely dominated by the spin-rotation mechanism so that empirical values of the cross sections for rotational angular momentum transfer σ_J are obtained as a function of temperature.

Nuclear spin relaxation measurements in the gas phase can be interpreted to provide quantitative information about the anisotropic part of the intermolecular potential. Data now available for CO interacting with rare gases, H_2, HX, and CO, and to a lesser extent for CO in N_2, O_2, CO_2, CH_4, and CF_4 provide the incentive for a potential energy surface determination by multiparameter fitting. These include beam scattering cross sections,[1] pressure broadening,[2] transport properties,[3] and spectra of van der Waals molecules.[4] We contribute to these the cross sections for rotational angular momentum transfer which are derived from nuclear spin relaxation by the spin-rotation mechanism.

EXPERIMENTAL

The samples were prepared as we have customarily done for previous work involving density- and temperature-dependent studies of the nuclear shielding. Measured amounts of isotopically enriched CO ($>90\%$ ^{13}CO) and buffer gas are completely frozen into the sample tube and sealed off. Total densities are between 5 and 40 amagat.

Temperatures were routinely regulated from 220 to 420 K with a precision of <0.5 °C, determined using ethylene glycol and methanol. All ^{13}C spin relaxation measurements were carried out using the standard inversion recovery technique on an IBM WP-200SY (4.6 T) spectrometer. Pulse sequences of the form π-τ-$\pi/2$ were used with $\geq 5T_1$ between sequences. The derived T_1's were within 0.5% of each other in all cases if the data analysis explicitly includes the $\tau \sim 0$ $(3\times 10^{-7}$ sec) peak intensity in the usual first-order rate equation

$$\ln\{(A_\infty - A_\tau)/(A_\infty - A_0)\} = -\tau/T_1 + \epsilon, \qquad (1)$$

where A_0, A_τ, A_∞ are peak intensities at delay times, 0, τ, and $\geq 5T_1$, respectively. These plots were routinely obtained and inspected. Usable data has no noticeable curvature, a small relative standard deviation in the slope (about 1%), and ϵ very close to zero.

If collisions are independent the spin-rotation relaxation time in a mixture of probe (CO) and buffer (B) molecules is additive as follows:

$$T_1 = \rho_{CO}(T_1/\rho)_{CO,CO} + \rho_B(T_1/\rho)_{CO,B}. \qquad (2)$$

We verified this relationship in mixtures of CO with Xe for mole fractions of CO varying from 0.02 to 0.5. Furthermore, we have verified this type of relationship for ^{13}C relaxation in CO_2 in mixtures with the entire set of buffer gases except O_2, the results of which will be reported elsewhere. Therefore, in our subsequent work we use this empirically verified form for cases in which the spin-rotation mechanism is the overwhelmingly dominant relaxation mechanism. Given that Eq. (2) is valid, the procedure for extracting $(T_1/\rho)_{CO,B}$ from the data becomes straightforward.

Typical data for ^{13}C in pure CO taken at several temperatures are shown in Fig. 1. Here T_1/ρ as a function of

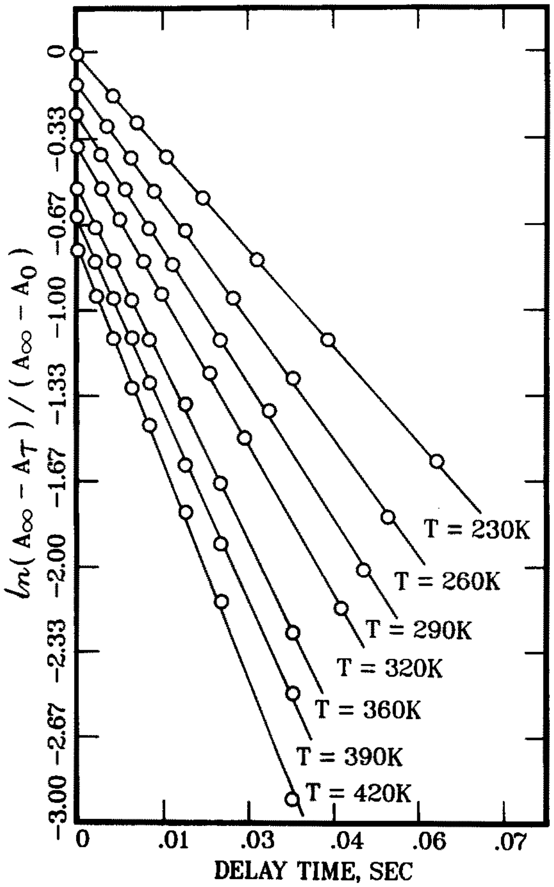

FIG. 1. Typical data for ^{13}C inversion recovery experiment in pure $^{13}C^{16}O$ gas at various temperatures. (The ordinate of each curve has been displaced in order that the different curves can be displayed in the same figure.) The slope of each line is $-1/T_1$.

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TABLE I. ^{13}C relaxation times for CO in various buffer gas. $(T_1/\rho) = (T_1/\rho)_{300\ K}(T/300)^n$.

Buffer gas	T(K)	$(T_1/\rho)_{300\ K}$ (ms amagat^{-1})	n
CO	230–420	1.231 ± 0.030	-1.32 ± 0.03
Ar	220–420	1.097 ± 0.041	-1.11 ± 0.06
Kr	230–400	1.229 ± 0.036	-1.17 ± 0.06
Xe	260–420	1.342 ± 0.030	-1.25 ± 0.06
O_2	230–420	0.862 ± 0.023	-1.32 ± 0.05
N_2	220–415	1.151 ± 0.019	-1.62 ± 0.03
CO_2	290–420	1.880 ± 0.036	-1.17 ± 0.06
HCl	280–420	1.592 ± 0.012	-1.41 ± 0.02
CH_4	240–420	1.251 ± 0.038	-1.45 ± 0.06
SF_6	300–420	2.151 ± 0.047	-0.94 ± 0.07

temperature has been obtained and is shown in Table I for ten collision partners. Figure 2 is a plot of ln (T_1/ρ) vs ln T for CO in various buffer gases showing the best fit straight line for each.

CROSS SECTIONS FOR ROTATIONAL ANGULAR MOMENTUM TRANSFER

The relationship between the spin-lattice relaxation times and the correlation times of the intermolecular interactions depends on the detailed properties of the molecule. For a linear molecule such as CO, the relaxation rate associated with the spin rotation interaction is[5]

$$(1/T_1)_{SR} = (2C^2/3)(2I_0kT/\hbar^2)\tau_{SR}, \qquad (3)$$

where I_0 is the moment of inertia, C is the nonzero component of the spin-rotation constant tensor, $C_\perp$ in Hz, and τ_{SR} is the correlation time.

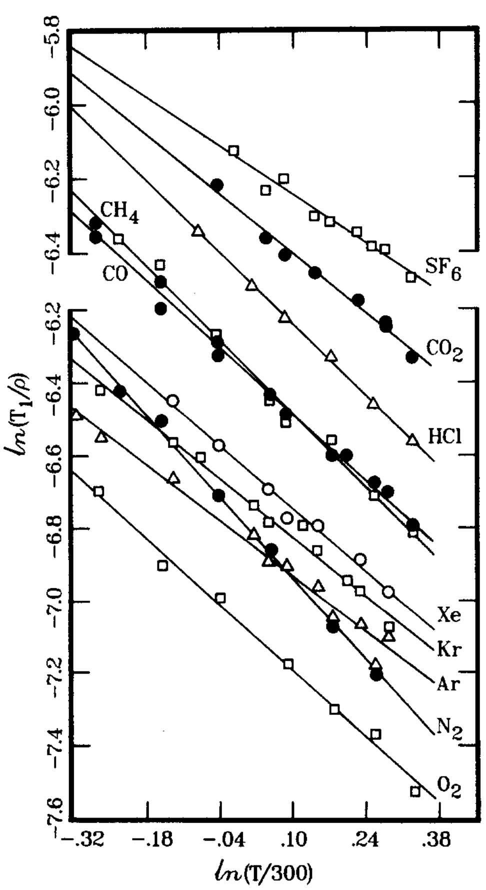

FIG. 2. The temperature dependence of (T_1/ρ) of ^{13}C in $^{13}C^{16}O$ in various gases in the extreme narrowing limit.

In the impact approximation, collisions are treated as instantaneous changes so that a correlation function at long times (times long compared to the duration of a typical binary collision) is specified by a given cross section for collisions which cause transitions between the magnetic substates

$$\tau_{SR} = (\langle \sigma_J v \rangle_{av}\,\rho)^{-1}, \qquad (4)$$

where v is the relative velocity of a pair of molecules. Thus, for a linear molecule

$$T_1/\rho = (3\hbar^2/4C^2I_0kT)(8kT/\pi\mu)^{1/2}\sigma_J. \qquad (5)$$

σ_J is a thermal average cross section which in the extreme narrowing limit can be identified with

$$\sigma_J = \frac{1}{2\langle \mathbf{J}^2 \rangle}\int_0^\infty \langle (\mathbf{J}_f - \mathbf{J}_i)^2 \rangle 2\pi b\, db$$
$$\equiv \frac{1}{2\langle \mathbf{J}^2 \rangle}\int_0^\infty \langle (\Delta \mathbf{J})^2 \rangle 2\pi b\, db. \qquad (6)$$

In Gordon's classical theory, $\mathbf{J}_i$ and $\mathbf{J}_f$ are the angular momentum vectors before and after the collision.[5] Gas phase spin rotational relaxation times are generally observed to vary as $T^{-3/2}$ and this has in fact been used as a reassuring indication of the dominance of the spin-rotation mechanism in relaxation. This implies that the thermal average cross section σ_J goes as T^{-1} usually, which means that the integral $\int_0^\infty \langle (\Delta \mathbf{J})^2 \rangle\, 2\pi b\, db$ is relatively independent of temperature. Empirical values of this integral in Eq. (6) can be obtained from every measured T_1 value for a linear molecule such as CO,

$$\frac{1}{2\langle \mathbf{J}^2 \rangle_{300}}\int_0^\infty \langle (\Delta \mathbf{J})^2 \rangle 2\pi b\, db, \text{Å}^2$$
$$= \sigma_J(T)(T/300) = \sigma_J(300)\{1 + a_1(T - 300)\},$$
$$= \kappa(T_1/\rho)(T/300)^{3/2}(\mu_{\text{CO-Buf}}/\mu_{\text{CO-CO}})^{1/2}, \qquad (7)$$

where $\kappa = (2/3)(10^{16}/L_0)\ (208.5/B_0)(2\pi C_\perp)^2\bar{v}_{300}{}^{-1}$, in which T_1 is in seconds, ρ is in amagat, $L_0 = 2.6872 \times 10^{19}$ mol cm^{-3}, B_0 is 1.8546 cm^{-1} for ^{13}CO,[6] 208.5 cm^{-1} is kT at 300 K, $C_\perp$ is -32.56 kHz[7], and $\bar{v}_{300}$ is the mean relative speed of CO molecules at 300 K in CO gas, in cm s^{-1}. In Fig. 3 we show the results of plotting Eq. (7) as a function of T for the CO-buffer pairs. The collision integral increases with increasing temperature for all pairs except CO with N_2. The data in Fig. 3 can be described by the parameter a_1 in Eq. (7).

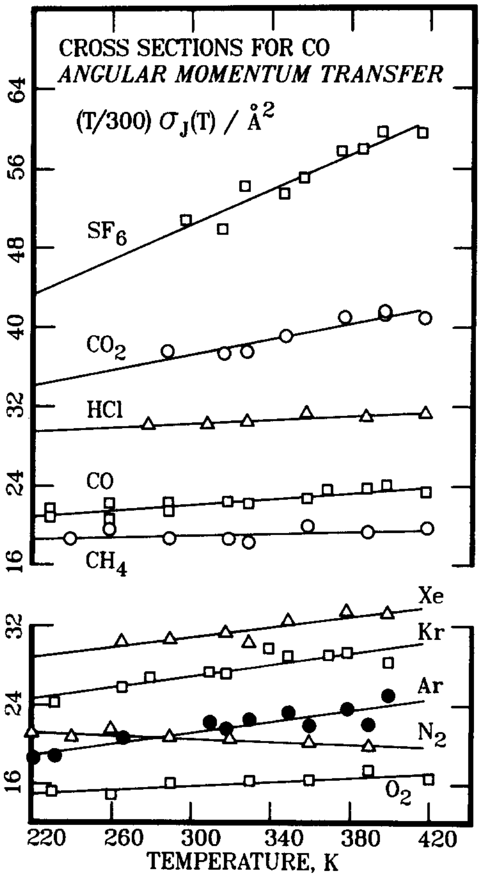

FIG. 3. The temperature dependence of the empirical values of $(2\langle J^2\rangle_{300})^{-1}\int_0^\infty\langle(\Delta \mathrm{J})^2\rangle\, 2\pi b\, db$ derived from T_1 experiments. [See Eq. (7).] These values are fitted to a linear equation $\sigma_J(300\,\mathrm{K})\{1+a_1(T-300)\}$ with no theoretical or physical basis, merely that the quality of the data over this limited temperature range does not justify any other descriptive functional form.

DISCUSSION

We have made the assumption that only the spin-rotation mechanism is important for $^{13}C^{16}O$ in the gas phase. The relaxation rate for the chemical shift anisotropy mechanism is given by[8]

$$(T_1^{-1})_{\mathrm{CSA}} = (2/15)(\omega\Delta\sigma)^2\tau_{\mathrm{CSA}}. \tag{8}$$

At densities in which the impact approximation is valid, all gas phase T_1 mechanisms can be considered to have correlation times $\tau = (\rho\bar{v}\sigma)^{-1}$, and the different cross sections are of the same order of magnitude. Using $\Delta\sigma = 402$ ppm,[9] and $\omega/2\pi = 50.2$ MHz for our experiments, gives

$$(T_1^{-1})_{\mathrm{CSA}}/(T_1^{-1})_{\mathrm{SR}} \simeq 6.8\times10^{-4}.$$

The relaxation rate for intermolecular dipole–dipole interaction for like spins is[10]

$$(T_1^{-1})_{\mathrm{DD}} = 8\gamma^4 I(I+1)\hbar^2\rho/\bar{v}r_0^2 \tag{9}$$

with r_0 being the molecular diameter. For $\rho = 10$ amagat,

$$(T_1^{-1})_{\mathrm{DD}}/(T_1^{-1})_{\mathrm{SR}} \simeq 1.6\times10^{-13}.$$

Thus, both the shielding anisotropy and the intermolecular dipole–dipole mechanisms can be neglected. ^{13}C relaxation in $^{13}C^{16}O$ in the gas phase can be interpreted as occurring strictly by the spin-rotation mechanism.

The data for ^{13}CO in paramagnetic oxygen as buffer gas is quite similar to that for other gases in Table I, except for its shorter relaxation times in comparison with other buffers. This implies that the spin-rotation mechanism for nuclear relaxation clearly dominates other mechanisms even in this case.

The cross sections compared to the geometric cross section πr_0^2 in Table II show that $(\sigma_J/\sigma_{\mathrm{geom}})$ is close to 1, indicating a relatively high efficiency of angular momentum

TABLE II. Cross sections for the transfer of angular momentum (rotational inelasticity plus molecular reorientation). The temperature dependence is fitted to the following form[a]: $\sigma_J(T) = \sigma_J(300\ \mathrm{K})\ (300/T)\{1+a_1(T-300)\}$.

Pair	$\sigma_J(300\ \mathrm{K})/\text{Å}^2$	a_1/deg^{-1}	σ_{geom}[b]$/\text{Å}^2$	$(\sigma_J/\sigma_{\mathrm{geom}})$
CO–CO	22.0 ± 0.5	1.3×10^{-2}	43.0	0.51
CO–Ar	21.1 ± 0.9	2.7×10^{-2}	39.0	0.54
CO–Kr	26.8 ± 0.9	2.8×10^{-2}	40.9	0.66
CO–Xe	30.8 ± 0.7	2.4×10^{-2}	44.7	0.69
CO–O$_2$	15.8 ± 0.4	9×10^{-3}	39.1	0.40
CO–N$_2$	20.5 ± 0.3	-8×10^{-3}	43.1	0.48
CO–CO$_2$	37.1 ± 0.7	3.7×10^{-2}	43.8	0.85
CO–HCl	30.2 ± 0.2	8×10^{-3}	37.0	0.82
CO–CH$_4$	19.0 ± 0.3	NIL	43.4	0.44
CO–SF$_6$	50.0 ± 1.2	8.6×10^{-2}	61.6	0.81

[a] Note that we have described $\{1+a_1(T-300)\}$ alternatively as $(T/300)^{3/2+n}$, where n is in Table I and a_1 is given above. These descriptions are equivalent within the scatter of the data shown in Figs. 2 and 3. In the idealized case when $n = -3/2$, a_1 is zero.

[b] The geometric cross section is $\sigma_{\mathrm{geom}} = \pi r_0^2$, where r_0 for the collision pair is calculated using the arithmetic mean of the r_0 values for CO and buffer molecule. The latter are taken from the following references: CO$_2$ and Ar: J. Kestin and S. T. Ro, Ber. Bunsenges. Phys. Chem. **86**, 948 (1982); Kr and Xe: J. Kestin, S. T. Ro, and W. A. Wakeham, J. Chem. Phys. **56**, 4119 (1972); CO and HCl: F. M. Mourits and F. H. A. Rummens, Can. J. Chem. **55**, 3007 (1977); N$_2$: M. Deraman, J. C. Dore, and J. G. Powles, Mol. Phys. **52**, 173 (1984); O$_2$: G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces, Their Origin and Determination* (Clarendon, Oxford, 1981); CH$_4$: N. Meinander and G. C. Tabisz, J. Chem. Phys. **79**, 416 (1983); and SF$_6$: J. Kestin and S. T. Ro, Ber. Bunsenges. Phys. Chem. **78**, 20 (1974).

transfer; every one or two collisions result in molecular reorientation or rotational inelasticity. This efficiency of angular momentum transfer appears to be high for the collision partners with large electrical moments (μ in HCl, θ in CO_2). With these exceptions, the efficiencies are in the same order as increasing polarizability of the collision partner. The *relative order* of the spin-relaxation cross sections for various buffers in Table II is the same as for pressure-broadening cross sections.[2]

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[1] H. P. Butz, R. Feltgen, H. Pauly, and H. Vehmeyer, Z. Phys. **247**, 70 (1971); A Kuppermann, R. J. Gordon, and M. J. Coggiala, Discuss. Faraday Soc. **55**, 145 (1975); J. Andres, U. Buck, H. Meyer, and J. M. Launay, J. Chem. Phys. **76**, 1417 (1982).

[2] J. P. Bouanich, J. Quant. Spectrosc. Radiat. Transfer **12**, 1609 (1972); A. Picard-Bersellini, R. Charneau, and P. Brechignac, J. Chem. Phys. **78**, 5900 (1983); J. P. Bouanich and C. Brodbeck, J. Quant. Spectrosc. Radiat. Transfer **13**, 1 (1973); R. B. Nerf and U. A. Sonnenberg, J. Mol. Spectrosc. **58**, 474 (1975); J. P. Bouanich and C. Haeusler, J. Quant. Spectrosc. Radiat. Transfer **12**, 695 (1972); P. Brechignac, A. Picard-Bersellini, and R. Charneau, J. Phys. B **13**, 135 (1980); P. Brechignac, A. Picard-Bersellini, R. Charneau, and J. M. Launay, Chem. Phys. **53**, 165 (1980).

[3] R. Afshar, S. Murad, and S. C. Saxena, Therm. Conduct. 17th, 295 (1981), Publ. 1983; E. N. Haran, G. C. Maitland, M. Mustafa, and W. A. Wakeham, Ber. Bunsenges. Phys. Chem. **87**, 657 (1983); N. Imaishi, J. Kestin, and W. A. Wakeham, Physica A **123**, 50 (1984); J. Kestin, S. T. Ro, and W. A. Wakeham, *ibid.* **119**, 615 (1983); R. D. Trengove, J. L. Robjohns, and P. J. Dunlop, Ber. Bunsenges. Phys. Chem. **88**, 450 (1984); J. Kestin and S. T. Ro, *ibid.* **87**, 600 (1983).

[4] W. G. Read and E. J. Campbell, J. Chem. Phys. **78**, 6515 (1983); A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle, and W. H. Flygare, *ibid.* **73**, 583 (1980); P. D. Soper, A. C. Legon, and W. H. Flygare, *ibid.* **74**, 2138 (1981); R. S. Altman, M. D. Marshall, W. Klemperer, and A. Krupnov, *ibid.* **79**, 52 (1983).

[5] R. G. Gordon, J. Chem. Phys. **44**, 228 (1966); **45**, 1635, 1649 (1966).

[6] B. Rosenblum, A. H. Nethercott, and C. H. Townes, Phys. Rev. **109**, 400 (1958).

[7] L. Ozier, L. M. Crapo, and N. F. Ramsey, J. Chem. Phys. **49**, 2314 (1968).

[8] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1961).

[9] D. B. Neumann and J. W. Moskowitz, J. Chem. Phys. **50**, 2216 (1969).

[10] I. Oppenheim and M. Bloom, Can. J. Phys. **39**, 845 (1961); F. M. Chen and R. F. Snider, J. Chem. Phys. **46**, 3937 (1967).