Isotope shift in the bulge effect of molecular scattering

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The recently observed "bulge" effect in rotationally inelastic scattering is substantiated by the detection of its isotope shift in K-CO collisions. This effect is a classical rainbow-type phenomenon which has been seen in the energy transfer or recoil-velocity dependence of K-CO and K-N_2 scattering at large angles and collision energies of about 1 eV. It is caused by the nonspherical bulge of the repulsive equipotentials of the intermolecular force and may be useful as a probe to its anisotropy.

INTRODUCTION

In a previous paper we reported on the observation of sharply structured recoil-velocity distributions of potassium atoms scattered rotationally inelastic from unoriented N_2 and CO molecules.[1] Single rotational transitions remaining unresolved, the distributions were specified in terms of a double-differential center-of-mass-system (CMS) cross section $J(u^*, \vartheta)$, with ϑ the CMS scattering angle and $u^* \equiv u'/u$ the quasicontinuous reduced CMS recoil velocity of the atom (dashes referring to "after collision"). The structure consists in nonvanishing J within rather well-defined u^* intervals extending from $u_0^* = 1$, elastic scattering, to values $u_i^*(\vartheta, E) < 1$ which correspond to a maximum of energy ΔE_i transferred into molecular rotation at a given angle and CMS collision energy E. At or very close to both the upper and the lower bound of this u^* interval the cross section exhibits a sharp maximum; moreover, at equal ϑ and E the interval of K-CO scattering is wider than for K-N_2, and a third maximum, missing for K-N_2, appears within its bounds. The experiments were done at large angles $\vartheta > \frac{1}{2}\pi$ and energies of about 1 eV. Therefore the scattering is dominated by the repulsive core of the interaction potential. We suggested a simple explanation of the observations: The rodlike structure of the essentially rigid molecule exposes two lever arms of equal (N_2) or unequal lengths (CO) to the incoming atom. Therefore, depending on impact parameter and molecular orientation, a single or two different maximal amounts of angular momentum and rotation energy may be transferred in the collision. If the intermolecular potential acted literally like a rigid bar, the maximal amounts would be transferred by hitting its ends perpendicularly; the u^* dependence of J would simply break off at maximum transfer. Actually the repulsive potential core has a bulge; as compared to a bar it will be better approximated by ellipsoidal-, egg-, or eight-shaped equipotentials. The bulge provides a coupling of the length of the equivalent lever arm with the direction of the impulse, which is independent of the direction of incidence. Owing to this coupling the *maximal* amounts of transferred angular momentum and energy will not only be approached as a function of impact parameter and molecular orientation, but will be *passed through*, thus giving rise to an (orientational) rainbow phenomenon, the "bulge maxima," in the recoil-velocity dependence of the cross section. Effects of this general origin had been predicted from formal arguments[2] shortly before they were observed in K-N_2 and CO scattering, and possibly also in other systems.[3]

The experiments, as well as a calculation of classical scattering from a rigid, initially nonrotating ellipsoid of revolution, indicate that under appropriate conditions the bulge maxima with their bright and dark sides may well be the dominant feature of rotationally inelastic scattering, and that they may eventually be useful as a direct and very sensitive probe of the (repulsive) anisotropy of the intermolecular potential. It is therefore the purpose of this paper to explore the effect further and thereby to substantiate its indicated explanation. The latter implies that the positions $u_{1,2}^*(\vartheta)$ of the two bulge maxima of K-CO respond to isotopic substitution. It will be shown that the replacement of natural CO by C ^{18}O indeed causes clearly detectable changes in the scattering.

In Sec. I we summarize the experimental conditions and the method of data acquisition. In Sec. II typical primary data are presented and approximately converted to cross sections, which are compared and evaluated on the basis of two crude, rigid-potential models in Sec. III.

I. EXPERIMENTAL

We prepared the collision partners in a conventional crossed-beam apparatus, using the seeding method on the K beam for increased collision energy, isentropic expansion to cool

TABLE I. Preparation and detection of collision partners.

Average K velocity	v_1 (m/sec)	3660(55)[a]
Relative velocity spread, FWHM[b]	$\Delta v_1/v_1$ (%)	17
Angular spread, FWHM	$\Delta\gamma_1$ (°)	0.25
Average CO velocity	v_2 (m/sec)	762(25)
Relative velocity spread, FWHM	$\Delta v_2/v_2$ (%)	18
Angular spread, FWHM	$\Delta\gamma_2$ (°)	5.7
K-CO relative velocity	$v=(v_1^2+v_2^2)^{1/2}$ (m/sec)	3740
K-CO collision energy	$E=\frac{1}{2}\mu v^2$ (eV)	1.18
CMS velocity of K before collision with CO	$u=m_2v/(m_1+m_2)$ (m/sec)	1560
Angular width of detector acceptance, FWHM	$\Delta\theta$ (°)	0.54
Velocity width of detector acceptance, FWHM	$\Delta v'/v'$ (%)	10

[a] Figures in parentheses throughout denote the ± uncertainty of the last given decimal place.
[b] I.e., "full width at half-maximum."

the CO beam, and in-plane detection by a Fizeau selector-Langmuir Taylor ribbon aggregate. No means of orientation of either partner are employed. Details have been given previously.[1] Relevant figures for these experiments are collected in Table I. The translational cooling of the CO beam, corresponding to a parallel temperature of 12 K, was found to be consistent with recoil-velocity distributions obtained in K-Ne scattering under corresponding stagnation conditions. The molecular rotation with an average angular momentum quantum number $\bar{j}=2.5\pm1$ before collision, equal for both isotopic CO species, is about two orders of magnitude slower than the repulsive-collision duration, and—like the vibration—contributes negligibly to the total energy in the collision. Both beams are virtually free of polymerization products. The potassium is vacuum distilled, the natural CO is 99.9% pure, and the $C^{18}O$ is 99% isotopically pure.

The Newton diagram of Fig. 1 indicates the kinematic situation of the experiments. In comparing the scattering off the two isotopic species all externally controllable parameters were kept as nearly equal as possible. Then, equal stagnation pressures at the CO beam nozzle produce average CO beam velocities in the laboratory system (LS), which differ by a factor $[m(C^{18}O)/m(CO)]^{1/2}$, or by 3.5%. Besides this the mass difference will also cause 3.9% differences in the initial CMS velocities of the partners, and 3.7% differences in the collision energy. The imperfections of the initial preparation and the detector, i.e., finite widths with respect to velocity and angle of the incoming distribution functions as well as detector acceptance functions, may be combined into two particularly significant quantities, $\Delta u^* = \Delta u'/u$ and $\Delta\vartheta$, which are measures of the resolving power of the experiment with respect

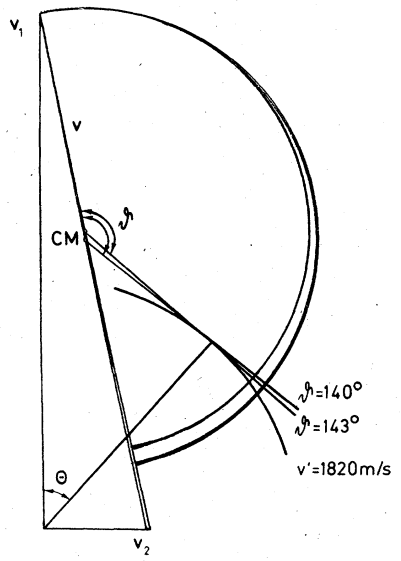

FIG. 1. Newton diagram showing the kinematics of K-CO and K-$C^{18}O$ collisions in a typical experiment in which the detector swings through LS angles θ accepting scattered K atoms at a fixed velocity v'. In the CMS it essentially scans recoil velocities in the neighborhood of a stationary angle $\vartheta=140°$ for K-CO or $\vartheta=143°$ for K-$C^{18}O$.

to reduced recoil velocity and angle in the CMS.[4] Both Δu^* and $\Delta\vartheta$ vary considerably over the CMS. The quantity Δu^*, which is more important for this experiment attains minimal values as low as 0.05 in the CMS region of $130° \lesssim \vartheta \lesssim 160°$, $u^* \gtrsim 0.6$ because several of the smearing effects partially compensate each other here. Therefore the observations are restricted to this CMS regime.

As may be seen by inspection of Fig. 1, this offers another advantage: of the two simple modes of data acquisition, i.e., scanning LS velocities at fixed LS angle θ, or LS angles at fixed LS velocity v', the latter—at appropriate v'—will make a CMS angle ϑ stationary.[5] If the stationary point falls in the u^* range of interest, the measured LS angular distribution at fixed v' will correspond very closely to the CMS recoil-velocity distribution at fixed ϑ. From previous experiments the angle dependence of the latter distribution is known and weak at large ϑ. Thus the "θ scan at fixed v'" mode of operation renders the desired item directly at a level of accuracy which is amenable to later corrections. As the cost of the isotopic material severely limits the measuring time, this mode was chosen as the most rapid one among others employing interpolation or such as have been used previously. Again, the two isotopic species will be compared at exactly the same (constant) LS velocity v' accepted by the detector. Figure 1 shows that this will make two slightly different CMS angles ϑ stationary, the smaller one relating to the heavier isotope. Also this discrepancy of about 3° is small and can be corrected for.

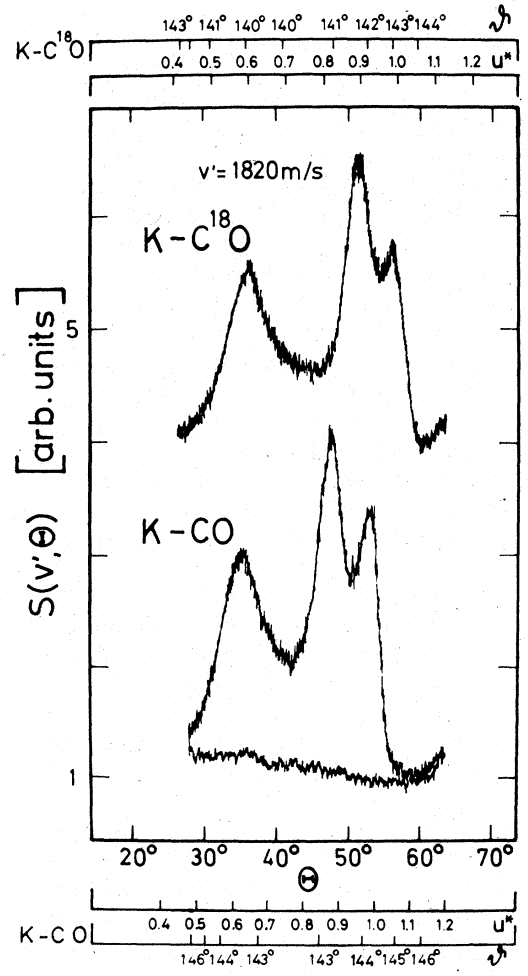

FIG. 2. Scattering signal S ($v' = 1820$ m/sec; θ) of K atoms recoiling from the two isotopic CO variations as a function of the LS angle θ. The additional abscissa scales giving the corresponding CMS variables u^*, ϑ are different for K-CO (below) and K-C^{18}O (above). The isotope effect shifts the two inelastic bulge maxima farther apart for K-C^{18}O. This may be directly read from the primary data by comparing the two recordings.

II. MEASURING RESULTS AND CROSS SECTIONS

Typical primary data are shown in Fig. 2. The two recordings represent the flux $S(v', \theta)$ of K atoms into the detector which are scattered from natural CO and from the isotopic variation C^{18}O (upper curve) at the same constant LS velocity $v' = 1.82 \times 10^3$ m/sec as a function of the LS angle θ. A run-back trace (at the bottom) was taken between the two experiments with K and natural-CO beams on, but not crossed. It shows the background under full beam load. Its short time average is used as the zero of the natural-CO signal and, with the appropriate offset, also as the C^{18}O-signal zero, which was not recorded for reasons of time.[6] For each CO species the LS variables v' and θ are converted into the corresponding CMS variables u^* and ϑ on additional abscissa scales. This is done in the "fixed velocity" approximation from a Newton diagram according to the average values of the initial preparation (Table I) and the detector settings v' and θ. As expected, ϑ is stationary at slightly different values for the two recordings. Except for the LS-CMS intensity transformation, the latter give very nearly the desired CMS recoil-velocity dependence of the cross section at constant ϑ. The dominating features of rotationally inelastic, repulsive K-CO scattering, described in the introduction, are clearly seen. For both isotopic variations one of the maxima appears close to $u^* = 1$, elastic scattering. The other two result from the action of two "bulged lever arms of different lengths" in the excitation of this molecule. Their separations on the u^* scale from each other or from the respec-

tive near-elastic maxima are different for natural CO and C ^{18}O, thus verifying a change in the lengths of both lever arms by isotopic substitution. This is the main result of this paper. It will be unaffected by the mostly negligible corrections which put both recordings on a scale of equal and exactly constant ϑ and equal collision energy.

One is naively tempted to associate the left, more inelastic maximum of each trace with scattering from the farther outsticking C end of the molecule, and the less inelastic central maximum with its O end. This presupposes that with respect to the molecular center of mass the range of the repulsive core of the intermolecular potential sufficiently conforms to the nuclear geometry of the molecule. The isotope effect confirms this. As is directly read from Fig. 2, shifting the molecular center of mass towards the O end in C ^{18}O results in less inelastic O-end and more inelastic C-end scattering.

For further discussion the LS-CMS conversion of the data of Fig. 2 is completed in Fig. 3. The double-differential CMS cross section $J(u^*, \vartheta\,|\,\bar{j}, E)\,du^*\,d\omega$ describes the transition of

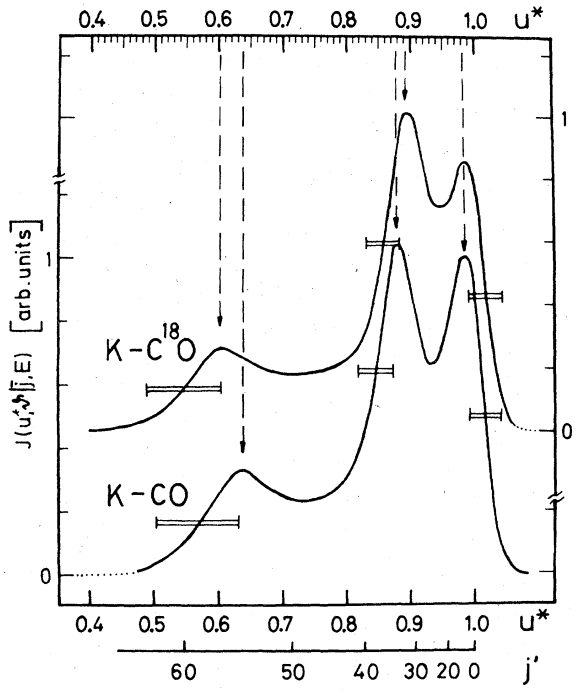

FIG. 3. Normalized CMS cross section $J(u^*, \vartheta \simeq \text{const}$ (2.5; 1.18 eV) obtained with Eq. (1) from the primary data of Fig. 2. The scattering angle is stationary at $\vartheta = 142.7°$ for K-CO and at $\vartheta = 139.9$ for K-C^{18}O, varying by about $+2°$ within the former, by approximately $+4°$ within the latter distribution. The arrows indicate the maxima positions evaluated in Table III.

the system from an initial preparation with collision energy E (or relative velocity $\vec{v} = \vec{v}_1 - \vec{v}_2$, $E = \frac{1}{2}\mu v^2$) and a distribution of unoriented molecular rotation with average angular momentum quantum number $\bar{j}$ to a final situation in which the detected partner 1 is scattered by ϑ (as measured against $\vec{v}$) into the CMS solid-angle element of velocity space $d\omega$ with reduced velocity $u^* = u'/u$ in the interval $du^* = du'/u$. In the fixed-velocity approximation, which is sufficient for the purpose of this paper, J is related to the recorded detector signal $S(v', \theta)$ by

$$S(v', \theta) = (\text{const})v'(v'/u')^2 u J(u^*, \vartheta\,|\,\bar{j}, E) = (\text{const})J/u^{*2}. \tag{1}$$

The first line results from the general multiple-integral relation between S and J by taking the distribution functions of the initial-preparation and the detector-acceptance functions as δ functions at the average values of Table I or the detector-angle settings θ of Fig. 2. The constant includes the fixed geometry of the apparatus as well as the product $n_1 n_2 v$ of particle densities of both beams in the scattering volume and the relative velocity. Of the extra factors v' takes account of the constant *relative* velocity spread transmitted by a Fizeau selector, $(v'/u')^2$ is the LS-CMS Jacobian of the quasicontinuous approximation, and u results from the use of reduced rather than absolute recoil velocities. In the second line all factors, which remain unchanged in a single run of these experiments, are absorbed into the constant. Fig. 3 shows the cross section J which results from Eq. (1). The highly inelastic parts of the curves are really much less populated in the collision than appears in the LS. The general structure of the u^* dependence of S remains, however, as do its characteristic differences due to the isotope effect.

In Fig. 3 an additional abscissa scale gives the final angular momentum quantum number j', which is calculated from u^* by

$$j' = [(E/B)(1 - u^{*2}) + (j + \tfrac{1}{2})^2]^{1/2} - \tfrac{1}{2},$$

with $j = \bar{j} = 2.5$, the average initial j of these experiments, and B the rotational constant of CO from Table II. The major portion of the curves corresponds to high rotational excitation. For C ^{18}O the j' values would be higher by 2.5% owing to the smaller B. As no unfolding has been done in this LS-CMS conversion, all the experimental smearing is carried over into the CMS results. As mentioned above a careful estimate of the CMS velocity-resolving power Δu^* has been made. This quantity is shown in Fig. 3 as error bars at several u^* values. It has been noted pre-

TABLE II. Properties of collision partners and the scattering situation.

Average equilibrium distance of K-CO potential[a]	r_m (10^{-8} cm)	4.9
Average well depth of K-CO potential[a]	ϵ (meV)	<9
de Broglie wavelength of free relative K-CO motion	$\lambda\!\!\!^{-}=\hbar/\mu v$ (10^{-10} cm)	1.04
Scattering parameter	$A=r_m/\lambda\!\!\!^{-}$	471
Reduced collision energy	$K=E/\epsilon$	>130
Largest observed energy transfer corresponding to $u^*=0.6$	$\Delta E=(1-u^{*2})E$ (eV)	0.76
Reduced translation energy after collision corresponding to $u^*=0.6$	K'	>47
Estimate of collision duration	$\tau_c\sim 0.2r_m/v$ (10^{-14} sec)	2.6
Rotational constant[b] of $^{12}C^{16}O$	B_e (meV)	0.2395 (1.931 39 cm^{-1})
Classical rotation period of CO before collision, i.e., for $\bar{j}=2.5$	$\tau_{rot}=[2cB_e(j+\frac{1}{2})]^{-1}$ (10^{-12} sec)	2.9
Inertial factor of K-CO of K-$C^{18}O$	μ/I (10^{16} cm^{-2})	1.869 1.851
Vibrational constant[b] of $^{12}C^{16}O$	ω_e (eV)	0.2691

[a] Reference 1.
[b] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1950), Vol. I.

viously that there is a close parallelism without exception between the varying Δu^* and the widths of the maxima or of their shadows slopes (i.e., the right slope of the elastic, and the left slopes of the inelastic maxima). These features of the true underlying cross section must be even sharper than they appear in Fig. 3.

Several other comparative runs at the same collision energy and other angles $130°<\vartheta<160°$ support the data and conclusions of Figs. 2 and 3.

III. DISCUSSION

Table II summarizes some data pertinent to the scattering situation and collision partners of these experiments. Very large A values and large observation angles, $\vartheta>1$ rad, satisfy a necessary requirement for classical scattering. With high initial and final reduced translation energies $K, K' \gg 1$ in addition, an overwhelming influence of the repulsive core of the intermolecular potential on the outcome of the collision is guaranteed. The molecular rotation before collision is very slow and contributes negligibly to the total energy. Its ratio to the collision duration is of the order of 10^2, giving rise to extremely sudden encounters and a wide spectrum of excited rotation after collision. This qualifies the terminology of "scattering by the C- or O-end" of a diatomic molecule. The vibration has been found in Ref. 1 to remain inactive, although the energy would suffice to excite up to four quanta. All these conditions are very much the same as in the previous experiments, the main results of which could be understood in terms of the simple assumptions of *classical* scattering from a *rigid*, initially nonrotating potential shell. It will therefore be instructive in a qualitative, perhaps crudely quantitative sense to compare the predictions of this simple model also with the present observations. Two model results of interest are: (i) The u^* dependence of the orientation-averaged cross section $J(u^*, \vartheta \mid 0, E)$ exhibits integrable singularities $i=0, 1, 2, \ldots$ at values

$$u_i^*(\vartheta)=[(1-A_i^2\sin^2\vartheta)^{1/2}+A_i\cos\vartheta]/(1+A_i)\,. \quad (2)$$

Here the A_i are products of the relevant inertial parameter μ/I of the system (μ: atom-molecule reduced mass; I: molecular moment of inertia) and the square of a linear dimension of the potential shell, which is a measure of its deviation from spherical symmetry. The determination of the u^* positions of the singularities at a given angle ϑ thus yields direct information on the latter property. This may prove to be a very important benefit of rotationally inelastic scattering as a probe of the intermolecular interaction. (ii) Specifically, for a potential shell taken to be a prolate ellisoid of revolution with

TABLE III. Parameters of ellipsoidal-model potential.

		$u^*_{i\,\max}$	u^*_i	$c-a$ (10^{-8} cm)	$z_0/(1+a/c)^{1/2}$ (10^{-8} cm)	z_0 (10^{-8} cm) for $c=2.5\times10^{-8}$ cm
K-CO	$i=0$	0.982(5[a])	1.000(5)			
	1	0.878(5)	0.860(5)	0.298(4)	0.086(4)	0.118(5)
	2	0.637(10)	0.600(10)			
K-C^{18}O	$i=0$	0.982(5)	1.000(5)			
	1	0.893(5)	0.875(5)	0.305(4)	0.104(4)	0.142(5)
	2	0.602(10)	0.568(10)			

[a]Errors relate to the estimated $u^*_{i\,\max}$ reading errors alone.

semiaxes a and c ($>a$), and a distance z_0 between its center of symmetry and the molecular center of mass,

$$A_0=0,\quad A_{1,2}\cong\frac{\mu}{I}\left(c-a\mp\frac{z_0}{\sqrt{1+a/c}}\right)^2; \tag{3a}$$

z_0 is measured along the internuclear axis of the molecule, which coincides with the axis of revolution of the ellipsoidal shell. From Eq. (3a) it is seen that $A_0=0$, gives rise to a singularity at $u_0^*=1$ for elastic scattering independent of angle. Besides this there will be two other singularities, a less and a more inelastic corresponding to A_1 and A_2, respectively. Their u^* positions are essentially determined by the "anisotropy" $(c-a)$ and the "excentricity" z_0 of the shell, which express the deviation from spherical symmetry of this simple potential model. The approximate expression for $A_{1,2}$—valid for "small" $z_0\ll4(c-a)(1+a/c)$—is good to better than 2% for the parameter values of interest here, and depends little on a third parameter, e.g., on c if—as will be the case here—the anisotropy is small compared to c. For the even simpler model of adjoining segments of two spheres with centers on the internuclear axis, displaced by $z_1, z_2(>z_1)$ in opposite directions from the molecular center of mass,

$$A_{1,2}=(\mu/I)z_{1,2}^2 \tag{3b}$$

is independent of the radii $r_{1,2}$ of the spheres, if $|r_1^2-r_2^2|<(z_1+z_2)^2$. The elastic singularity is missing in this case.

To use Eqs. (2) and (3a) or (3b) for a comparative evaluation of model parameters from the data of Fig. 3, the experimental resolving power Δu^*, slightly different collision energies (see Table I), and not exactly constant and equal angles ϑ (see Fig. 2) for the two isotopic species must be accounted for. A finite resolving power will turn a cross section singularity into a maximum of finite height displaced towards the bright side of the singularity by an amount δu^* which depends on the resolving power and was found by test calculations to be $\delta u^*=0.32\,\Delta u^*$ for these experiments. Columns 1 and 2 of Table III give the u^* positions of the maxima and of the corresponding hypothetical classical singularities of the cross sections of Fig. 3, the latter being obtained by the indicated correction. In both cases the ellipsoidal-model result $u_0^*=1$ is met within the quoted error limits. For K-CO the energy and angle dependence of $J(u^*,\vartheta=\text{const})$ have been studied previously. Under the conditions of these experiments both are weak and in rough accord with the predictions of the rigid-shell model, i.e., Eq. (2) with regard to angle. Nonconstant and unequal ϑ are therefore taken care of by their use in Eq. (2) to obtain the A_i. Finally, corrections to reduce the u_i^* to equal energy for both isotopic species are found to be negligible.

Equation (3a) then gives the anisotropy $c-a$ as well as the values of $z_0(1+a/c)^{-1/2}$ of Table III. As c (or a) remains undetermined in these experiments, the excentricity z_0 is quoted for the arbitrary choice $c=2.5$ Å. At the energy of the experiments this may be a reasonable value to simulate the range of the real interaction effective in large-angle scattering. But z_0 will not change outside its quoted error limits for any other $c>1$ Å.

The model indeed "explains" the observed isotope effect as a shift of the molecular center of mass by $\Delta z_0=(0.024\pm0.007)\times10^{-8}$ cm with respect to the intermolecular force field, the anisotropy of which remains virtually unaltered. The real effect is a shift by 0.032 Å.

Although the discrepancy between the real center-of-mass shift and its model value is very small, the fact that it is outside the error limits of the latter may be significant. It will be noted that the value $z_0=0.118$ Å for K-CO shows the center of the ellipsoidal potential shell not to be located halfway between the CO nuclei, but shifted by about 0.037 Å towards the C end, the distance

of the molecular center of mass from the midpoint between the nuclei being only 0.081 Å. Knowing the origin of the bulge maxima, we may relate this latter model result to the attempt to evaluate the K-CO scattering using a potential of the wrong symmetry, i.e., $D_{\infty h}$ of the ellipsoid instead of $C_{\infty v}$ for K-CO. Apparently the geometry of the equipotentials of the real interaction is such as to produce higher torque at the molecular C end beyond what is afforded by an inversion symmetric force field and an inertia-determined reference point. The too-small isotope effect of z_0 has conceivable the same origin.

The evaluation of the two-spheres model [Eq. (3b)] yields

$$\text{CO: } z_1=0.212(4)\ \text{Å}, \quad \text{C}^{18}\text{O: } z_1=0.201(4)\ \text{Å},$$
$$z_2=0.384(6)\ \text{Å}, \qquad z_2=0.409(6)\ \text{Å},$$

where the figures in parentheses denote the uncertainty of the last decimal place. As indicated above these numbers are independent of the radii of the spheres, contrary to the magnitude of $J(u^*)$, which will strongly depend on them. Although this model does not produce the elastic singularity or maximum which is observed, it shows that (i) two centers simulating maximal rotational excitation are in a distance on the order of, but less than the equilibrium bond length $r_e=1.128$ Å of CO; that (ii) there is an isotope effect which is quantitatively too small, but assigns the indices 1, 2 to the O and C atoms, respectively, and that (iii) again the details of the real anisotropy are simulated by ratios z_2/z_1, which do not correspond to the atomic distances from the molecular center of mass, but favor the carbon atom.

In conclusion, it is seen that analysis leads to statements about size or accuracy of linear dimensions of the colliding systems which are of the order of the de Broglie wavelength of its free relative motion (see Table II). Although it is true that the bulge effect exploits the "resolving power" of the scattering process more fully than do many other features of atomic scattering, the comparative meaning of such statements should be observed. The quoted errors arise from the $u^*_{i\,\max}$ reading errors alone, which are treated as of statistical nature. The other major sources of uncertainty, i.e., selector calibration factors, resolving-power corrections, wave effects in the results, and the deficiency of Eq. (3a), will be very nearly the same for both isotopes and are *not* considered in Table III and the two-spheres-model evaluation. The total error of a u_i^* is estimated to be three times that given in the table.

While their isotope shift qualitatively supports the interpretation of the bulge maxima, a more realistic description is needed to make full use of the power of this phenomenon in molecular scattering.

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[1]W. Schepper, U. Ross, and D. Beck, Z. Phys. A 290, 131 (1979).

[2]L. D. Thomas, J. Chem. Phys. 67, 5224 (1977).

[3]K. Rudolph, J. P. Toennies, J. Chem. Phys. 65, 4483 (1976); W. Eastes, U. Ross, J. P. Toennies, Chem. Phys. (to be published).

[4]Δu^* is defined as the full width at half-maximum of the calculable distribution of reduced CMS recoil velocities which results from the distributions of the initial preparation and the detector acceptance on the assumption of a CMS cross section which is constant with respect to angle and a δ function with respect to recoil velocity. $\Delta\vartheta$ is correspondingly defined.

[5]At such a stationary point the LS *angle* resolving power of the detector determines—among others—the CMS *velocity* resolution and vice versa. This is part of the reason for Δu^* values as low as 0.05 in this CMS region.

[6]The recorded CO background varies slowly and almost linearly with angle, and is reasonably constant in time. The $C^{18}O$ signal appears as if it sat on a background less variable with angle. It was, therefore, also evaluated on the alternative assumption of constant backgroung. The resulting changes in peak locations on the u^* scale turned out to be negligible. The rise of both signal traces at $\theta > 60°$ is also common to the background. It has nothing to do with the investigated process.