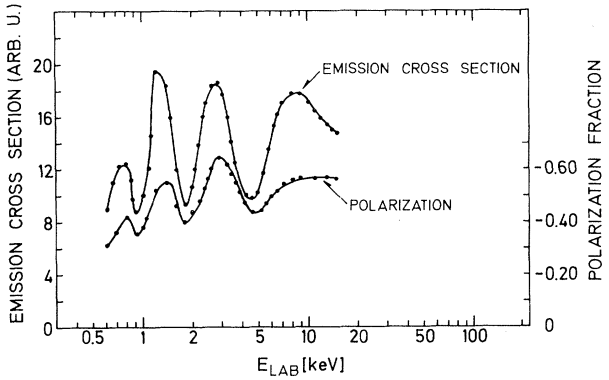

FIG. 3. Cross sections and negative polarizations plotted as a function of the ion-beam energy for the Ne I 6266-Å radiation from the p_5 level for the Na^+-Ne system.

pendent oscillations present in the total excitation cross section for the p_5 level can be accounted for nearly exclusively by the mechanism responsible for the polarization. This is not the case for the oscillations present in the light emitted from the p_1 level, a $^1S_0$ term not exhibiting polarization.

The present data show that for systems such as O^+-Ne or Na^+-Ne, for which the ground states are $L=0$ states, the rotational coupling responsible for the population of the $L=1$ excited states in Ne may act in a very selective manner.

The polarization data show that for $L=1$ states, the magnetic sublevels with $m=\pm 1$ are populated much more than the $m=0$ sublevel and are thus mainly responsible for oscillations present in the total-excitation cross sections. A further, more detailed analysis of the polarization data for the N^+-Ne, O^+-Ne, Na^+-Ne, and Mg^+-Ne systems will be presented in a subsequent paper together with more detailed data on all the systems investigated.

Added note.—Independent observations of strong polarization effects in the Na^+-Ne low-energy collisions have been performed by Tolk *et al.*[5]

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Rotational Effects in Collisionally Induced Fine-Structure Transitions*

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Cross sections for transitions between the $P_{3/2}$ and $P_{1/2}$ levels of cesium induced by collisions with isotopes of methane are found to be several orders of magnitude larger than with krypton, with which one might expect similar interaction potentials. This enhancement is explained by a semiclassical theory in terms of Fourier components which arise from the rotation of CH_4 and which lie close to the transition frequency. The theory predicts the experimentally found isotope effect.

The importance of rotational effects in determining rates of vibrational relaxation has been established recently.[1] In this paper we present what we believe to be the first experimental and theoretical evidence of a strong rotational enhancement of collisionally induced nonadiabatic electronic transitions.

The particular collision process is

$$\mathrm{Cs}(6p\,^2P_{3/2}) + \mathrm{CH}_4 \rightarrow \mathrm{Cs}(6p\,^2P_{1/2}) + \mathrm{CH}_4,$$

where CH_4 is one of the deuterated isotopes of methane. Collisions with Rb(5p) in place of Cs(6p) have also been studied, as have collisions with other molecules. We restrict consideration here to collisions of Cs with methane isotopes.

Methane is a small, relatively inert, spherical-top molecule with a polarizability ($17.5a_0^3$) close to that of Kr ($16.7a_0^3$). One might reasonably expect alkali-CH_4 interaction potentials and collision cross sections to be similar to those for alkali-Kr. However, the cross section for CH_4 is about 10^5 times larger than for Kr.[2] The lowest-lying vibrational levels of methane, at roughly 1000 cm^{-1}, are not energetically accessible during the thermal-energy collisions of the present experiment [fine-structure splitting in Cs($6p$) is 554 cm^{-1}], so that the great enhancement must be due to rotational degrees of freedom and related nonspherical interactions between the alkali and methane. A theory capable of explaining this enhancement is sketched below.

In an impact-parameter treatment, the cross section for the transition $1 \leftarrow 2$ is given by

$$\sigma_{12} = 2\pi \int_0^\infty db\, b |S_{12}|^2, \tag{1}$$

where b is the impact parameter and S_{12} an element of the scattering matrix $\underline{S}$. In the exponential approximation,[3] time ordering of factors in the expression for $\underline{S}$ is ignored and we can write

$$\underline{S} = \exp(-i\underline{\mathcal{V}}), \tag{2}$$

where the elements of $\hbar\underline{\mathcal{V}}$ are Fourier transforms of matrix elements of the interaction:

$$\hbar\mathcal{V}_{ij} = \int_0^\infty dt \exp(i\omega_{ij}t) V_{ij}(t). \tag{3}$$

Here $\hbar\omega_{ij}$ is the energy separation of states i and j. If only two states are considered ($i, j = 1, 2$), the exponential expression [Eq. (2)] can be worked out explicitly, giving

$$|S_{12}|^2 = |\mathcal{V}_{12} \sin\mathcal{V}_D/\mathcal{V}_D|^2, \tag{4}$$

$$|\mathcal{V}_D|^2 \equiv |\mathcal{V}_{12}|^2 + \tfrac{1}{4}|\mathcal{V}_{11} - \mathcal{V}_{22}|^2. \tag{5}$$

In the case of collisions with noble gases, this theory interprets the small cross sections in terms of small Fourier amplitudes [Eq. (3)] at the transition frequency. The transition appears to occur principally between the $B^2\Sigma$ and $A^2\Pi_{1/2}$ states,[4] and the major contribution to the Fourier amplitude arises from the turning-point region in the $B^2\Sigma$ state. A simple relation exists in this case between $|V_{11} - V_{22}|^2$ and $|V_{12}|^2$; namely, it can be shown that[4]

$$|V_{12}|^2 = 2|V_{11} - V_{22}|^2. \tag{6}$$

An estimate with realistic potentials[4] from Eqs. (1)–(6) does indeed yield small cross sections with a strong positive velocity dependence as found experimentally.[2,5]

The interaction with methane differs in several respects from that with Kr. In particular, methane has an octupole moment which interacts with the third spatial derivative of the electrostatic potential of the alkali core plus valence electron.[6] The octupole interaction with the alkali P states falls off as R^{-6} at large distances and depends on the orientation of the molecule with respect to the internuclear axis. Because we treat the rotation classically, the interaction $V_{12}(t)$ has Fourier components at multiples of the rotation frequency ω; harmonics from the first to the fifth are present. The R^{-6} octupole interaction couples the two $A\Pi$ states together; coupling to the $B\Sigma$ state is not as strong. At average rotational energies near room temperature the fifth harmonic terms lie closest to resonance and dominate the interaction in Cs. Consequently, in Eq. (3) we put

$$V_{12}(t) \simeq R^{-6} \sum_{m=1}^{5} C_m e^{+im\omega t} + \text{c.c.}, \tag{7}$$

where C_m is the (possibly complex) coefficient for the mth harmonic term, and after substitution into Eq. (3), noting $R(t) = R(-t)$, we find

$$\hbar\mathcal{V}_{12} \simeq 2 \sum_{m=1}^{5} C_m \int_0^\infty dt\, R^{-6} \cos(m\omega t - \omega_{21}t). \tag{8}$$

In the results presented below, we consider for simplicity only the dominant ($m = 5$) harmonic term.

Evaluation of $\mathcal{V}_D$ is greatly simplified by ignoring transitions occurring at internuclear separations larger than $R_C \simeq (11 \text{ or } 12)a_0$. Because of the strong R dependence of V_{12} and the attractive nature of the Π potentials,[4] this approximation seems well justified. We can then take the molecular Π states occurring at R_C (averaged over methane orientations) as our unperturbed basis. For these states $\hbar\omega_{21} \simeq \frac{2}{3}\Delta E$, where ΔE is the atomic fine-structure separation.[4] Also, since primarily the zero-frequency (i.e., orientation averaged) component contributes to $\mathcal{V}_{ii}$, $\mathcal{V}_{11} - \mathcal{V}_{22} \simeq 0$.

The resultant expression for $|S_{12}|^2$ [Eq. (4)] is a function of the rotational frequency ω of methane which is strongly peaked near $\omega \simeq \omega_{21}/m$. The thermal average over ω of σ_{12} [Eq. (1)] thus gives

$$\bar{\sigma}_{12} \equiv (2/\sqrt{\pi}) \int_0^\infty dy\, y^{1/2} e^{-y} \sigma_{12} \simeq 2\sqrt{\pi}(m/\omega_{12}) y_0^{3/2} e^{-y_0} \int_0^\infty db\, b \int_{-\infty}^{\infty} d\omega \sin^2|\mathcal{V}_{12}|, \tag{9}$$

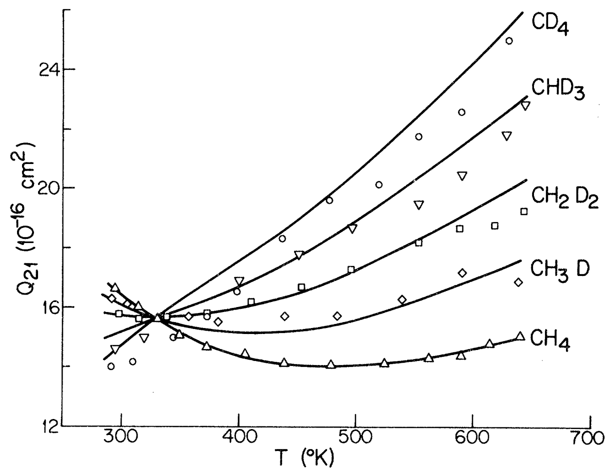

FIG. 1. Cross sections for transitions $^2P_{3/2} \rightarrow {}^2P_{1/2}$ in the $6p$ state of Cs in collisions with isotopes of methane. The solid lines are the theory, for which the potential parameters have been adjusted to fit the undeuterated-CH_4 data.

where $y = \frac{1}{2}\omega^2/kT$ and $y_0 = I\omega_{12}^2/2m^2kT$. $\bar{\sigma}_{12}$ is averaged over initial translational energies for comparison with the experimental values Q_{21}. A statistical factor of $\frac{1}{2}$ has been introduced since only one of the two molecular states arising from the atomic $P_{3/2}$ level contributes significantly to the transition. The strong dependence on the molecular moment of inertia I, contained in the factor $y_0^{3/2}e^{-y_0}$, gives a fairly pronounced isotope dependence. The factor $\sin^2|\mathcal{V}_{12}|$ depends somewhat on the reduced mass μ of the colliding pair, but since μ increases by not more than 25% in going from CH_4 to CD_4, whereas I is doubled, most of the isotope effect is contained in the factor $y_0^{3/2}e^{-y_0}$.

To calculate the remaining part of the expression, the Π potential, which determines the trajectory, was represented by a curve with four adjustable parameters. The parameters were adjusted to fit the experimentally determined cross sections of undeuterated CH_4. Cross sections for the other methane isotopes are then calculated as indicated above. The results are plotted in Fig. 1.

The measurements were made by determining ratios of sensitized to resonance fluorescent intensities with an apparatus similar to that of Czajkowski and Krause[7] and over a temperature range 290–640°K. The resulting thermally averaged cross sections, $Q_{21}(P_{3/2} \rightarrow P_{1/2})$ and $Q_{12}(P_{1/2} \rightarrow P_{3/2})$, are believed accurate to better than 10%.[8] Detailed balance was satisfied in the ratios of Q_{21}/Q_{12} to within 4%.

The theoretical and experimental results are seen to agree quite satisfactorily. We have, of course, made several approximations in the theory, but most seem well justified for the Cs interaction with methane. In particular, the classical treatment of molecular rotation is supported by the experimental results for the partially deuterated methanes, which lie between those for the spherical molecules CH_4 and CD_4. Furthermore, the use of classical trajectories (not straight, however!) is made more plausible by the occurrence of the transition between the two Π states, which run nearly parallel to one another.

On the basis of the good agreement with experiment, especially in predicting the correct isotope effect, and the reasonable values of the parameters obtained,[9] we conclude from the theory that the large enhancement in cross section for fine-structure transition in collisions with methane, in comparison to that with Kr, results mainly from the rotation of the methane and its resultant coupling of the alkali states with Fourier components of the interaction which lie close to the transition frequency.

Further details of the experiments and of the theoretical calculation will be reported shortly.

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[9] The form chosen for the potential was designed to facilitate the calculation and fitting of the cross sec-

tions, and the parameters are not readily identifiable with simple qualities of the potential. They nevertheless indicate a Π-state well with a depth of about 2000 cm^{-1}, the repulsive wall of which begins to have negative curvature above about 1000 cm^{-1} above the top of the well.

Inertial-Range Spectrum of Turbulence*

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We argue that the value of μ in Kolmogorov's energy spectrum formula $E(k) \propto k^{-5/3-\mu}$ cannot be deduced from general principles. The argument is supported by exhibiting a modified Navier-Stokes equation which has the same dimensionality, symmetries, invariances, and equilibrium statistical ensembles as the original but gives a drastically different inertial range.

Kolmogorov's formula for the inertial-range spectrum of high-Reynolds-number, incompressible, three-dimensional, Navier-Stokes (NS) turbulence is

$$E(k) = C\epsilon^{2/3}k^{-5/3}(kL)^{-\mu}. \qquad (1)$$

Here $E(k)$ is the wave-number spectrum of kinetic energy, C is a dimensionless parameter of order 1, ϵ is the rate of energy dissipation by viscosity, per unit mass, and μ is a parameter which is zero in Kolmogorov's 1941 theory[1] and >0 in the modified theory of 1962.[2,3] Equation (1) applies to the inertial range of wave numbers $L^{-1} \ll k \ll k_d$, where L is the macroscale, at which energy is fed into the turbulence, and $k_d = (\epsilon/\nu^3)^{1/4}$ (ν is the kinematic viscosity) is the approximate wave number where dissipation becomes strong.

The 1941 theory assumes that the inertial-range wave numbers exhibit an energy cascade, from low wave numbers to high, which is (a) local in wave number; (b) characterized by self-similar statistical distributions at all inertial-range scales; and (c) dependent on the macroscale statistics only through ϵ. The 1962 theory invokes a modified picture in which there is a self-similar increase in spatial intermittency of the velocity differences $\vec{u}(\vec{x}+\vec{r}) - \vec{u}(\vec{x})$ ($|\vec{r}| \sim 1/k$) at each cascade step, resulting in increasing efficiency of energy cascade as k rises.[4-6] The parameter μ also appears in other, related predictions of the 1962 theory. The latter is at least approximately supported by a variety of geophysical experiments, which consistently yield $\mu \sim 0.05$.[7-9] Measurements of $E(k)$ itself at high Reynolds numbers are consistent with (1), but cannot distinguish $\mu = 0$ from $\mu \sim 0.05$.[10,11]

Equation (1) has not been derived from the NS equation in any solid way, and the difficulties in trying are severe and well known.[6] This situation makes attractive some recent speculations by Martin[12] and Nelkin[13] that (1) can be validated, and μ determined, from general statistical-mechanical principles, based on dimensionality, invariances, and symmetries, without the need of calculations involving the detailed structure of the NS equation. In particular, Martin and Nelkin point out the possibility of an analogy between μ and the universal exponents of critical-point phenomena.

Such suggestions should be pursued. But we think it timely to make a counterargument of fundamental nature, based on the fact that the inertial-range cascade is a state of strong departure from absolute statistical equilibrium and thereby differs qualitatively from states of thermal fluctuation about absolute equilibrium.

The NS equation in a cyclic box of side $\gg L$ may be written

$$(\partial/\partial t - \nu\nabla^2)u_i(\vec{x}) = -P_{ij}(\nabla)\{[\vec{u}(\vec{x})\cdot\nabla]u_j(\vec{x})\}, \qquad (2)$$

where $P_{ij}(\nabla)$ is the solenoid (transverse) projection operator, defined by

$$\begin{aligned} P_{ij}(\nabla) &= \delta_{ij} - \nabla^{-2}\partial^2/\partial x_i\partial x_j, \\ \nabla^{-2}f(\vec{x}) &\equiv -(4\pi)^{-1}\int f(\vec{x}')\,|\vec{x}-\vec{x}'|^{-1}\,d^3x'. \end{aligned} \qquad (3)$$

Under the transformation $\vec{u}(\vec{x}) = \sum \vec{h}(\vec{k})\exp(i\vec{k}\cdot\vec{x})$, (2) becomes

$$(\partial/\partial t + \nu k^2)h_i(\vec{k}) = -i(\delta_{ij} - k_ik_j/k^2)\sum_p h(\vec{k}-\vec{p})\cdot\vec{p}h_j(\vec{p}), \qquad (4)$$

where the sums are over all allowed wave num-